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# REPORT DOCUMENTATION PAGE

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14. ABSTRACT Conventional devices for energy generation and storage are typically designed and fabricated with two-dimensional multilayer structures of active and passive components. In recent years, researchers have recognized that marked improvements in performance can be achieved through the design and fabrication of materials and structures into three-dimensional (3D) architectures. Three-dimensional battery architectures, for example, enable one to achieve high energy density without compromising high power density. For solar cells, the highest efficiency to date was achieved using a vertically integrated 3D structured tandem solar cell, in which a triple-junction design covered the full solar spectrum. It is also anticipated that other 3D architectures, particularly in the nanoscale domain, will provide the next breakthrough in solar cell technology. This symposium addressed the challenges in design, fabrication and materials that comprise 3D configurations for energy generation and storage.				
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The topics covered in this symposium are related to energy conversion and energy storage, both of which represent areas of long term science and technology for the Navy and the Marine Corps. A central theme of the symposium, new materials and device geometries, is consistent with major thrusts at ONR. The symposium includes several sessions which relate to Navy interests including polymer and hybrid photovoltaics, multiple junction and 3D solar cells, and multiple sessions on 3D battery architectures covering the materials, designs, fabrication and operation.



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# Symposium P: Three-Dimensional Architectures for Energy Generation and Storage

April 14 - 17, 2009

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\* Invited paper

SESSION P1: 3-D Battery Architectures: From Design Concepts to Functional Devices  
Chairs: Bruce Dunn and Amy Prieto  
Tuesday Morning, April 14, 2009  
Room 2022 (Moscone West)

**8:30 AM \*P1.1**  
**Three-Dimensional Architectures: Establishing a New Paradigm for Power Source Materials and Device Design.** Michele L. Anderson, US Office of Naval Research, Arlington, Virginia.

The concept of three-dimensional (3D) power source architectures was proposed to challenge the paradigm of conventional

micrometer-scaled multilayer power source designs, which are limited by long ionic diffusion lengths and labor-intensive manufacturing. Understanding and controlling ion and electron transport and power source architectures at the nanoscale, and rational assembly of electroactive nanometer-scale structures, should allow for simultaneous increases in energy and power densities in energy-storage devices. Through major investments beginning in 2001, ONR facilitated the enabling science that has now established a new field of 3D power source architectures. Over the past eight years, progress in the theory of charge storage and transfer at the nanoscale has demonstrated the necessity of re-thinking the design paradigms for nanostructured devices. The development and demonstration of 3D power source architectures based on Si micromolded structures, self-assembly, macroporous templating, and origami, to name a few, have established the versatility of synthetic and fabrication techniques available for the embodiment of functional 3D architectures. This paper will summarize the history of 3D power source architectures for energy-storage applications, including the scientific challenges that have been overcome and those that remain, key theoretical insights that have influenced approaches to designing nanostructured power sources, significant milestones in 3D power source device demonstrations, and the future impact of this new scientific and technical field.

#### 9:00 AM \*P1.2

##### **Improving Centuries-Old Electrical Energy-Storage Devices by Rethinking Multifunction on the Nanoscale and in 3D**

**Debra R. Rolison<sup>1</sup>, Jeffrey W Long<sup>1</sup>, Lytle C Justin<sup>1</sup>, Jennifer L Dysart<sup>1</sup>, Anne E Fischer<sup>1</sup>, Katherine A Pettigrew<sup>1</sup>, Amanda J Barrow<sup>1</sup> and Jean M Wallace<sup>2</sup>; <sup>1</sup>Surface Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Nova Research, Inc., Alexandria, Virginia.**

Electrical energy storage in batteries and electrochemical capacitors (ECs) buoys any future success in the global effort to shift energy usage away from fossil fuels. A marked improvement in the performance of these power sources is critical for this effort, yet both are mature technologies that have always disregarded Moore's Law. Improved performance requires redesigning the reaction interphases in which occur the fundamental processes that store energy in batteries and ECs. Energy researchers are now rethinking the requisite multifunction—mass and charge transport, electronic and ionic conductivity, and electron-transfer kinetics—in light of nanoscience and architectural design in three dimensions [1,2,3]. The design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks for chemical, physical, and physicochemical charge storage will be highlighted, including the use of "nothing" (void space) and deliberate disorder as design components [4] as well as the importance of reexamining in a nanoscopic form those materials that yielded poor energy-storage performance when used in a macroscopic form. [1] J.W. Long, B. Dunn, D.R. Rolison, H.S. White, *Chem. Rev.* 104 (2004) 4463. [2] D.R. Rolison, J.W. Long, *Acc. Chem. Res.* 40 (2007) 854. [3] D.R. Rolison, J.W. Long, J.C. Lytle, A.E. Fischer, C.P. Rhodes, T.M. McEvoy, M.E. Bourg, A.M. Lubers, *Chem. Soc. Rev.* 12 (2009) in the press. [4] D.R. Rolison, *Science* 299 (2003) 1698.

#### 9:30 AM \*P1.3

##### **Towards High Energy Density 3D-integrated Lithium-Ion Microbatteries. Peter H.L. Notten and Jos Oudenhoven; Eindhoven University of Technology, Eindhoven, Netherlands.**

In our modern-day society electronics play an ever increasing role. Traditionally separate devices are used for lighting, control of temperature and entertainment. However, there is a strong tendency towards more complete and intelligent systems. A crucial role in this Ambient Intelligence is played by various sensing devices, preferentially Autonomous Devices, which combine a sensor function with wireless communication. To make independent operation possible an energy supply needs to be included. Energy can, for example, be harvested from photovoltaic cells, temperature differences, vibrations etc. To ensure a stable power supply, it is necessary to also include an energy storage device, for which all-solid-state lithium ion micro-batteries are a promising candidate. It has been shown that planar thin-film lithium ion batteries can successfully be produced, and that these show an excellent reversible electrochemical response [1]. To increase the energy density of these thin-film batteries a novel approach was proposed [2]. This concept is based on the etching of 3D structures into a silicon substrate, which increases the effective surface area of the thin film battery without increasing its footprint area in the device it is powering. Using this method an increase in energy storage capacity of a factor 25 is predicted [3]. Silicon wafers are common substrates in semiconductor industry, and also the anisotropic etching of several 3D geometries (e.g. pores, trenches and pillars) using reactive ion etching is a relatively mature technique [4]. The step conformal deposition of battery layers into these structures require non-line of sight techniques, which are on one hand established in the production of integrated devices, but are on the other hand still mostly unexplored for the deposition of battery materials. These methods include Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) [5]. In this presentation the concept of the 3D integrated battery will be discussed and the highlights in the investigations will be shown. The focus of this contribution will be on the exploration of CVD and ALD as deposition techniques for thin-film micro-batteries. Moreover, the (electro)-chemical characterization of several active battery layers will be discussed.

#### 10:30 AM \*P1.4

##### **Designing Architecture and Composition of Templated Electrodes For Energy Storage. Andreas Stein, Zhiyong Wang, Melissa Fierke and Anh Vu; Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.**

Targeting miniaturized batteries with sufficient geometric power and energy densities to support ultrasmall devices, we designed and developed interpenetrating electrochemical cell architectures based on three-dimensionally ordered macroporous (3DOM) electrode structures. We previously demonstrated the rate advantages of nanostructured, 3DOM carbon electrodes in half-cell designs and assembled a complete lithium ion electrochemical cell, in which a conformal electrolyte/separator coating on the surface of a 3DOM carbon anode isolated the anode from a continuous vanadia cathode phase that filled the remaining pore space. While reversible lithiation/delithiation was possible with this design, the capacity of the first prototypes was limited by the electronic resistivity of the two electrode components and ionic resistivity of the separator. To address these limitations we are studying the effects of architecture and composition of each cell component on its electronic and mechanical properties. In

particular, we will discuss the effects of carbon pore texture, composite formation of porous glassy carbon anodes with graphitic carbon, tin oxide or silicon, and doping of vanadia cathodes with ruthenia or silver on these properties.

#### 11:00 AM \*P1.5

**The Challenge of Modelling the 3D-Microbattery** Daniel Brandell, Vahur Zadin and John O Thomas; Materials Chemistry, Uppsala University, Uppsala, Sweden.

Parallel to current popular interest in novel battery technologies for large-scale applications (like EV/HEV/P-HEVs, UPS and renewable-energy storage), there is the somewhat less well publicized but no less pressing demand at the opposite end of the dimension-scale for miniaturized power sources to satisfy the ever-increasing needs of the microelectronics and bio-MEMS industries. Research into solid-state Li-based thin-film batteries has so far focused mainly on flat 2D-configurations, with their intrinsic limitations in performance. The need for better battery performance within a confined space has provoked the exploration of ways of exploiting the third dimension in so-called 3D-MB concepts, where Area Gain (A.G.) factors in excess of 40 are now considered realistic. A common feature of this research has been the implementation of novel 3D current-collector and electrode fabrication techniques to realize short ion-diffusion lengths and thereby high power densities. These efforts have often exploited nano-porous Al<sub>2</sub>O<sub>3</sub> templates; some practical examples will be given. In the design of such 3D-MB architectures (and not least in their subsequent device implementation), it is very clear that modelling has a vital rôle to play, especially since we are here exploring the nano-scale regime, where counter-intuitive electrochemical phenomena can appear. Clearly, atomic-level Molecular Dynamics (MD) simulation in combination with Finite Element Analysis (FEA) techniques will be especially relevant in this context. However, there is an underlying problem in their use: current upper space/time limits for standard MD methods lie in the range 10nm/10ns; while the FEA concept usually breaks down above these limits. We are currently endeavouring to bridge this gap, so that information derived from atomic-level MD can be used both to help pinpoint the types of local 3D-MB geometry which should be avoided - or encouraged - and also for use as input parameters to FEA to probe the performance of different micro-battery architectures. The FEA approach delivers information on overall system properties: heat flow, mass transport, stress energy, etc. Some relevant examples taken from our recent work involving the modelling of nano phenomena in 3D-MB design will be given; e.g., self-assembled short-chain polymer nano-coatings, nano-fillers, etc. The enhancement achieved has been characterized at the atomic level in our MD treatment, and this information then transferred to an FEA analysis of their implementation in nano- and microbattery architectures. Our work in this area and in its subsequent use in modelling real 3D-MB configurations will be described.

#### 11:30 AM P1.6

**High Volumetric Energy Density Microbatteries.** Can K Erdonmez<sup>1</sup>, Wei Lai<sup>1</sup>, Thomas F Marinis<sup>2</sup>, Caroline K Bjune<sup>2</sup>, Fan Xu<sup>3</sup>, Nancy J Dudney<sup>3</sup> and Yet-Ming Chiang<sup>1</sup>; <sup>1</sup>M.I.T., Cambridge, Massachusetts; <sup>2</sup>Draper Laboratory, Cambridge, Massachusetts; <sup>3</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Advances in microfabrication allow for the construction of compact, stand-alone systems integrating multiple device functionalities. Lack of accompanying power sources of similar size and sufficient energy density, however, has been a roadblock to proliferation of such devices. With decreasing size, all existing bulk battery designs exhibit rapidly decreasing energy density due to a growing fraction of packaging materials. While significant advances have been made in solid-state thin film batteries, many applications require other form factors to achieve areal power density requirements. Here, we demonstrate rechargeable batteries of ~ 5 mm<sup>3</sup> volume that exhibit energy densities exceeding those of commercial primary batteries 2 orders of magnitude larger in volume. Volumetric energy densities up to 650 Wh/L have been obtained at C/3 rates (~200 W/L) for packaged batteries. To our knowledge, such energy densities are unprecedented for batteries at the ~ mm<sup>3</sup> size scales. The high energy density corresponds to exceptionally high volumetric utilization by active materials, enabled by a thick 3D cathode design. Li<sub>1-x</sub>CoO<sub>2</sub> is used as the active cathode material for its high electronic conductivity across most of the composition range of interest, and metallic lithium is used as the anode. A novel packaging design was developed and will be discussed in the presentation.

#### 11:45 AM P1.7

**Probing Li-Ion Battery Electrode Architectures with a Focused Ion Beam and Modeling.** Arnold M Stux<sup>1</sup>, David J Rowenhorst<sup>2</sup>, Edward P Gorzkowski<sup>2</sup>, David E Stephenson<sup>3</sup> and Dean R Wheeler<sup>3</sup>; <sup>1</sup>Nanopower Research Labs, Rochester Institute of Technology, Rochester, New York; <sup>2</sup>Materials Science and Technology, Naval Research Laboratory, Washington, District of Columbia; <sup>3</sup>Chemical Engineering, Brigham Young University, Provo, Utah.

A dual beam Focused Ion Beam (FIB) has been used in conjunction with porous electrode modeling and modifications to electrode fabrication as an integrated effort to tune morphologies of Li-ion battery electrodes. Recent advances in automation, as well as computing power, have rendered serial sectioning a viable solution for determining the three-dimensional (3D) structure of complex microstructures. Using the ion beam, thin sections were milled from a Li-ion battery electrode while the electron beam was used for high-resolution imaging of the cross section. The information from the FIB can be entered into a model that describes the chemical, physical, and electronic phenomena. Porosity is a commonly used variable to characterize aggregate microstructure and morphology and is considered in the model. Pore structure and overall porosity affect ion and electron transport in combination with particle size and shape distributions. Micron- and submicron-size constituents can also influence transport in these electrode film architectures. We use 3D reconstruction techniques as a tool for further understanding of these morphologies. This opens up possibilities to develop more rigorous models and further understand the structure-performance relationships pertaining to ion and electron transport and surface reactions in porous battery electrodes. The development of these analytical and predictive techniques is envisioned for implementation into the materials and process design cycle for battery

electrodes.

#### SESSION P2: Multiple Junction and Novel Structure Solar Cells

Chair: Gang Li

Tuesday Afternoon, April 14, 2009

Room 2022 (Moscone West)

##### 1:30 PM \*P2.1

**Three-Dimensional Photovoltaic System Architecture for Very High Efficiency Modules.** Allen Barnett<sup>1</sup> and Christiana Honsberg<sup>2</sup>; <sup>1</sup>Electrical and Computer Engineering, University of Delaware, Newark, Delaware; <sup>2</sup>Electrical and Computer Engineering, Arizona State University, Tempe, Arizona.

Very High Efficiency Solar Cell (VHESC) modules are being designed and developed for portable applications. The design goal is for modules that operate at greater than 50 percent efficiency. The high-efficiency module is based on co-design of the optics, interconnects, and solar cells. Low concentration (5 to 20X) is used to capture much of the performance benefit of concentration, reduce the material costs and lead to systems with no moving parts (static concentrators). The new architecture significantly increases the design space for high-performance photovoltaic modules in terms of materials, device structures, and manufacturing technology. It affords multiple benefits, including increased theoretical efficiency, new architectures that circumvent material/cost trade-offs, improved performance from non-ideal materials, device designs that can more closely approach ideal performance limits, reduced spectral mismatch losses, and increased flexibility in material choices. The design approach focuses first on performance, enabling the use of existing state-of-the-art photovoltaic technology to design high performance multiple junction III-Vs for the high and low energy photons and a new silicon solar cell for the mid-energy photons, all while circumventing existing cost drivers through novel solar cell architectures and optical elements. Our approach is driven by proven quantitative models for the solar cell design, the optical design and the integration of the two. A test bed for rapid development and verification of performance of subsystems has been developed. The results and analysis of the first complete integrated optics and solar cells on this test bed shows module efficiency greater than 36%. Analysis shows a direct path to efficiencies greater than 40%. These initial results have not been verified by any 3rd party. We have previously reported the sum of the solar cell efficiencies to be over 42%, and optical subsystem efficiency greater than 93%. The new system architecture is based on a "parallel" or lateral optical concentrating system, which splits the incident solar spectrum into several bands and allows different optical and photovoltaic elements in each band. The optics and the solar cells are co-designed to achieve the maximum conversion efficiency of the module. The design rules, initial designs, solar cell and module results will be presented. The lateral solar cell architecture increases the choice of materials for multiple junction solar cells, by allowing the solar cell in each spectral band to be optimized independently of the others. In this way, the lattice and current matching constraints are reduced. Further, since the devices do not need to be series connected, spectral mismatch losses are reduced, which is important for tandems in terrestrial environments.

##### 2:00 PM \*P2.2

**Efficient Light Harvesting In Multiple-device Stacked Structure for Polymer Solar Cells.** Srinivas Sista<sup>1</sup>, Hsiang-Yu Chen<sup>1</sup>, Jianhui Hou<sup>2</sup>, Vishal Shrotriya<sup>2</sup>, Gang Li<sup>2</sup>, Yan Yao<sup>1</sup> and Yang Yang<sup>1</sup>; <sup>1</sup>Materials Science & Engineering, University of California-los angeles, Los Angeles, California; <sup>2</sup>Solarmer Energy, Inc., El Monte, California.

Efforts are being made to increase the efficiency of polymer solar cells. One of the strategies to increase the efficiency is to make use of tandem architecture. In this presentation we will discuss a multiple-device stacked structure in which two polymer solar cells are stacked together and are connected either in series or parallel for efficient light harvesting. The two sub cells of the stacked structure were based on poly(2-methoxy-5, 2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV). The bottom cell has a multilayer transparent conducting layer made of a lithium fluoride (LiF)/ aluminium (Al)/ gold (Au), so that the unabsorbed photons can be transmitted through and absorbed by the top cell. The stacked structure showed an almost doubled open circuit voltage (VOC) when connected in series and doubled short circuit current (JSC) when connected in parallel. We extend this concept to stacked cells with sub cells made from two different polymer blend systems. The two polymers are chosen such that one is a low band gap polymer and the other a large band gap polymer. This results in an increase in absorption range and a larger part of the solar spectrum is covered. We expect to achieve very high efficiencies from this multiple-device stacked structure.

##### 2:30 PM P2.3

**Absorption Enhancement In Si Wire Arrays for Photovoltaic Applications.** Michael David Kelzenberg, Jan A Petykiewicz, Morgan C Putnam, Josh M Spurgeon, Daniel B Turner-Evans, Chaitanya Rastogi, Brendan M Kayes, Michael A Filler, Nathan S Lewis and Harry A Atwater; California Institute of Technology, Pasadena, California.

Photovoltaic devices based on arrays of vapor-liquid-solid (VLS) grown Si nano- or micro-wires are being investigated as potential low-cost alternatives to wafer-based Si solar cells. A fundamental requirement is that they absorb nearly all above-bandgap photons in the solar spectrum. While others have observed and simulated light absorption in VLS-grown Si nanowires for photovoltaic applications [1,2], our prior experimental data and simulations [3] indicate that, for the 2-10  $\mu\text{m}$  minority carrier diffusion lengths observed in our wires, optimal photovoltaic efficiency favors substantially larger wire diameters than previously studied. For this reason we have characterized the optical absorption of several Si wire arrays to study the effects of incident beam angle and wavelength, wire dimensions, long-range and short-range order in the wire array lattice, packing fraction, and the metal catalyst tips. Si wires were grown by a photolithographically-patterned VLS process which produced high-fidelity arrays of

vertical Si wires over several mm<sup>2</sup>. Wires of 3 μm nominal diameter and 80 μm nominal length were patterned in quasi-random, quasi-periodic, and periodic lattices with packing fractions ranging from 4.9% to 17%. The as-grown wire arrays were then encased in a transparent PDMS polymer; peeled intact from the Si growth substrate, and transferred upside-down to a quartz slide to enable substrate-free observation the reflection and transmission of light through the wire arrays. Optical absorption measurements were performed from 460-1800 nm in a custom designed absorption apparatus featuring an integrating sphere assembly capable of angular rotation, with swept monochromatic illumination provided by a supercontinuum laser. The absorption spectra of each Si wire array were compared in terms of the percentage of photons, within the above-bandgap spectral range considered, that would be absorbed from the AM 1.5G spectrum. For the arrays studied, this ranged from 17% to 58%, representing an absorption enhancement of 2.3 to 3.5 times the geometrical packing fraction alone, or a spectral enhancement of 3 to tens of times that expected from planar Si slab of equal volume as the wires comprising the array. Although none of the wire arrays absorbed as much as an efficient Si solar cell, this result has two potentially useful implications for Si wire array-based photovoltaics. Firstly, it suggests that full absorption might be achievable with higher but physically realizable packing fractions. Secondly, this absorption enhancement could increase injection levels within a photovoltaic device by reducing the volume of Si; which could enable higher efficiencies analogous to light trapping or optical concentration in planar photovoltaic devices. [1] Tsakalakos, L., et. al. Journal of Nanophotonics 2007 [2] Hu, L.; Chen, G. Nano Lett. 2007 [3] Kelzenberg, M., et. al. 33rd PVSC

#### 2:45 PM P2.4

**Efficient Photovoltaic Devices Employing Ternary PbS<sub>x</sub>Se<sub>1-x</sub> Nanocrystals.** Wanli Ma, Joseph Luther, Haimei Zheng, Yue Wu and Paul Alivisatos; Chemistry, UC Berkeley, Berkeley, California.

Solar power, as one of the most abundant and easily accessible energy sources, has attracted more and more interests. In recent years, extensive studies have been carried out to search for novel photovoltaic materials with easier processing abilities and large-volume production potentials, such as semiconducting polymers and inorganic colloidal nanoparticles. Compared to polymer/fullerene composites, colloidal quantum dots (QD) can have increased infrared photon harvesting and improved charge transport due to their tunable bandgap and highly crystalline structures. Among them, low bandgap lead chalcogenides with superior carrier mobilities are currently the most promising photovoltaic QD materials. PbS and PbSe QD based solar cells have already obtained reasonable efficiency of 1.1%~2.1% due to large photocurrent densities. Recently, ternary QD based on cadmium and lead chalcogenides have been synthesized and studied. However, the utilization of novel alloyed QD in solar cells has not yet been systematically reported. In order to investigate the photovoltaic property of ternary QD, we synthesized monodispersed and highly crystalline PbS<sub>x</sub>Se<sub>1-x</sub> nanoparticles with different selenium and sulfur composition ratios. According to the observation of high resolution TEM with elemental mapping, selenium and sulfur were uniformly distributed in each QD, which indicated the formation of alloyed ternary nanoparticles. Rutherford Back Scattering Spectra were recorded to investigate the actual elemental composition ratios of nanoparticles in comparison with the precursor ratios used during QD synthesis. When studying the optical properties, we observed the gradual absorbance and photoluminescence (PL) spectra changes with different selenium and sulfur ratios in alloyed nanoparticles. The PL and PL lifetime measurements indicated that alloyed QD had less surface charge traps and hence better transport property. The photovoltaic properties of ternary nanoparticles were thoroughly investigated. Schottky junction solar cells with a structure of ITO/QD/Al were fabricated and tested under standard AM 1.5 illumination conditions. PbSe based solar cells had higher short circuit current (ISC) while PbS devices had larger open circuit voltage (VOC). Compared to pure PbSe and PbS QD, improved VOC and ISC were both obtained for PbS<sub>x</sub>Se<sub>1-x</sub> QD based devices. At a certain sulfur to selenium ratio, the best photovoltaic performance has achieved a current density of 16mA/cm<sup>2</sup>, a Voc of 0.45eV, a fill factor of 50%, and an energy conversion efficiency of 3.5%. This is the highest efficiency obtained so far for colloidal QD based solar cells. Our photovoltaic devices were fabricated at room temperature without any sintering process. This efficiency can be further improved with P-N junction architectures. The better performance of ternary QDs is assumed to arise from the reduced surface traps and improved QD/metal interface energy band alignment.

#### 3:30 PM \*P2.5

**Future Terrestrial III-V Multijunction Solar Cells: Practical Efficiency Ceiling and Technology Pathways** Daniel Law<sup>1</sup>, Richard King<sup>1</sup>, Hojun Yoon<sup>1</sup>, Melissa Archer<sup>2</sup>, Andreea Boca<sup>1</sup>, Christopher Fetzer<sup>1</sup>, Shoghig Mesropian<sup>1</sup>, Taka Isshiki<sup>1</sup>, Kenneth Edmondson<sup>1</sup>, Dhananjay Bhusan<sup>1</sup>, William Hong<sup>1</sup>, Harry Atwater<sup>2</sup> and Nasser Karam<sup>1</sup>; <sup>1</sup>Boeing - Spectrolab, Sylmar, California; <sup>2</sup>California Institute of Technology, Pasadena, California.

Increasing number of concentrator photovoltaic systems being built now use III-V multijunction cells, due to the high efficiency levels that this cell technology achieved. The rapid growth in cell efficiency and its strongly leveraging effect to lower system cost are enabling system manufacturers to produce concentrator systems competitive with other technologies and offering potential cost advantages. It is important to keep pushing the theoretical efficiency ceiling through the use of better band gap combinations in future multijunction cell designs to reach still higher efficiencies. First-principle efficiency limits are examined for current and potential solar cell architectures under the terrestrial spectrum. The fundamental loss mechanisms of non-absorption of low-energy photons, thermalization of electrons and holes to their respective band edges, and the difference between band edge energies and quasi-Fermi levels are quantified and contrasted for selected cell designs. Spectrolab is developing technology pathways for future high efficiency terrestrial multijunction cells in several research and development programs, with the goals of reaching average production concentrator cell efficiencies of 40% in 2010, and 43% by 2015. These future terrestrial concentrator cells will likely utilize new technology approaches such as highly metamorphic materials, inverted crystal growth, direct-wafer bonding, 4- or more junction architectures, and their combinations to achieve the desired bandgaps while maintaining excellent device material quality for optimal solar energy conversion. Recent experimental results will be discussed for prototype terrestrial concentrator cells using an upright metamorphic approach, as in the 40.7% efficient cell, 4-junction GaInP/ AlGaInAs/ GaInAs/ Ge terrestrial concentrator cells, metamorphic ~1-eV subcells & inverted GaInP/ 1.4-eV GaInAs/ 1.0-eV GaInAs 3-junction structure, and multijunction cells on wafer-bonded, layer transferred epitaxial templates.

**4:00 PM P2.6**

**Outdoor characterisation of High Efficiency Luminescent Solar Concentrators for Smart Windows** Mauro Pravettoni<sup>1,2</sup>,  
 Rahul Bose<sup>2</sup>, Amanda J Chatten<sup>2</sup>, Robert P Kenny<sup>1</sup> and Keith W Bamham<sup>2</sup>; <sup>1</sup>Institute for Energy - Renewable Energy Unit,  
 European Commission DG JRC, Ispra, Varese, Italy; <sup>2</sup>Blackett Laboratory, Imperial College London, London, United Kingdom.

Luminescent Solar Concentrators (LSCs) have been studied since 70s [i] and typically consist of glass or transparent polymer slabs, doped with organic dyes that act as luminescent centres. Incident light is partially absorbed, re-radiated by luminescent species and then partially total-internal-reflected towards the edges of the slab, where photovoltaic cells are glued to convert light in electricity. Interest in LSCs has recently grown thanks to recent reports of high efficiency devices [ii]. The increase in lifetimes of organic dyes together with some results in the production of inorganic luminescent species such as quantum dots or quantum rods helped also to boost the development in this technology. The high efficiency value of 7.1% was measured in 2008 at the European Solar Test Installation, Joint Research Centre of the European Commission (Ispra, IT) and reported in literature [iii]. Due to their own nature, LSCs convert both direct and diffuse radiation to electrical power [iv]: no tracking system is necessary and therefore they represent a potentially cheap solution, complementary to conventional concentrating systems, particularly well-fitted to building integration. In this work we present recent results in outdoor current/voltage characterisation of LSCs, with particular highlight of the performance under various irradiating conditions. The impact of the presence of a backside reflector on the module efficiency is also highlighted. [i] W. H. Weber - J. Lambe, Appl. Optics 15, 2299 (1976). [ii] M. J. Currie et al., Science 321, 226 (2008). [iii] L. H. Sloof et al., Phys. Stas. Sol. (RRL), to be published (online Sep 29 2008). [iv] M. Pravettoni et al., Proc. 23rd EU PVSEC, Valencia (2008).

**4:15 PM P2.7**

**Atomic Layer Deposition of Copper Sulfides for 3-D Photovoltaic Devices.** Qiaoer Zhou<sup>2</sup>, Lily Yang<sup>1</sup>, Tong Ju<sup>1</sup> and G. B. Aleris<sup>1</sup>; <sup>1</sup>Physics, University of California, Santa Cruz, Santa Cruz, California; <sup>2</sup>Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California.

Photovoltaic devices with nanostructured TiO<sub>2</sub> electrodes and an inorganic absorber layer of Cu<sub>x</sub>S deposited with atomic layer deposition (ALD) have been constructed and tested. The goal is to combine the high surface area and enhanced scattering of a porous electrode with a very thin conformal inorganic absorber deposited by a surface-controlled ALD technique. The incorporation of self-assembled quantum dots onto the TiO<sub>2</sub> surface is also being investigated to harvest electrons from multiple-exciton generation within the quantum dots. The basic un-optimized solar cell devices used a heterojunction structure of glass/ITO/sol-gel TiO<sub>2</sub>/porous-TiO<sub>2</sub>/ALD Cu<sub>x</sub>S/P3HT/Au. The purpose of the thin layer of spin coated P3HT is to collect the holes and prevent shorting. The porous TiO<sub>2</sub> layer was deposited with a solution of ~40nm or ~100nm nanoparticles of TiO<sub>2</sub>, baked at 100C and then sintered at 450C. A hydrogen plasma treatment of the TiO<sub>2</sub> was evaluated for the removal of residual carbon from the surface and to facilitate nucleation of the ALD layer. A b-diketonate-type metal-organic compound Cu(thd)<sub>2</sub> and H<sub>2</sub>S were used as precursors for ALD deposition. The temperature dependence of the growth rate was determined for films deposited on corning glass, silicon, TiO<sub>2</sub> sol-gel films and TiO<sub>2</sub> nanoparticle (NP). The films deposited at low temperature had low resistivity of 1x10<sup>-3</sup> ohm-cm. The resistivity increases as samples were annealed at 250C or by depositing films at higher temperature. The absorption data showed that films with a thickness of 12nm had a bandgap of 1.6eV making them ideal for efficient photovoltaic response. AFM analysis indicated that the film deposited at low temperature had polycrystalline morphology with a grain size of ~50nm and a film roughness of ~1nm. SEM showed conformal coating of a 300nm thick layer of TiO<sub>2</sub> nanoparticle network formed with ~40nm nanoparticles. The penetration of the Cu<sub>x</sub>S into the TiO<sub>2</sub> matrix was complete forming a solid composite structure of Cu<sub>x</sub>S wth an embedded TiO<sub>2</sub> electrode matrix. Results for the optimization of open circuit voltage and short circuit current will be presented.

**4:30 PM P2.8**

**Three-dimensional Carbon Nanotube Based Photovoltaics.** Jack David Flicker<sup>1</sup> and Jud Ready<sup>2,1</sup>; <sup>1</sup>Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia.

The production of cheap energy from the sun will be a major research objective in the coming years. Major strides must be made in solar cell efficiency, including increasing the absorbance efficiency of a cell by etching or texturing. In order to increase the absorbance efficiency of solar cells, we have developed a three dimensional solar cell structure by depositing a cadmium telluride thin film overtop carbon nanotube towers. These towers act as both a scaffolding and electrical interconnect. Multiple photon interactions as they reflect between these towers increase the absorption efficiency. We have developed a theoretical model and computer simulation to maximize the number of photon interactions due to the geometrical characteristics of the system (aspect ratio, spacing, size, shape, etc). Simulated modeling has shown that by optimization of parameters a three dimensional cell can obtain up to a 300% increase in power production over traditional planar cells.

**4:45 PM P2.9**

**Three-Dimensional Quantum Dot Supra-Crystals for Photovoltaic Energy Conversion.** Qinghui Shao<sup>1</sup>, Alexander A Balandin<sup>1</sup>, Alexander I Fedoseyev<sup>2</sup> and Marek Turowski<sup>2</sup>; <sup>1</sup>Nano-Device Laboratory, Department of Electrical Engineering and Materials Science and Engineering Program, University of California - Riverside, Riverside, California; <sup>2</sup>CFD Research Corporation, Huntsville, Alabama.

Three-dimensional (3D) ordered arrays of quantum dots - quantum dot supra-crystals (QDS) - where the role of atoms is played by quantum dots - have been shown to benefit the thermoelectric energy conversion [1-2]. The potential of 3D regimented QDS in thermoelectrics is related to mini-band formation for both electrons and acoustic phonons in way similar to photonic crystals. In this talk we argue that 3D supra-crystals can be beneficial for the photovoltaic (PV) energy generation by serving as intrinsic layers in the intermediate-band (IB) solar cells. It was predicted that IB solar cells have the PV efficiency for energy conversion exceeding the Shockley-Queisser limit for a single junction cell of ~33%. The IB energy level helps to collect photons with the energy less than the band gap of the host material, which allows one to improve the short-circuit current without degrading the open-circuit voltage. QDS with appropriately tuned parameters such as dot size, inter-dot distance, shape and barrier height, can act as the IB solar cell material. The QDS parameters have been determined using the first-principle theory [3]. It has been found that the energy spectra of the electrons and holes in the ordered QDS are distinctively different from those in the single quantum dots or conventional quantum-well superlattices. The charge-carrier dispersion and charge localization are very sensitive to the quasi-crystallographic directions defined by the dots. The analysis of the PV solar cells performance was carried out on the example of the InAsN/GaAsSb material system. By calculating the actual electron dispersion for different QDS we were able to select the quantum dot parameters, which place the first electron mini-band, i.e. subband, in the band-gap region at the energy suitable for this mini-band to serve as the IB energy level [4]. Using the detailed balance theory we determined the efficiency of such QDS-based IB solar cells. The upper-bound theoretical PV efficiency for QDS with the quantum-dot size of ~5 nm is substantially higher than the theoretical efficiency for a single-junction single-band material. This work has been supported by the AFOSR contract FA9550-07-C-0059 and NASA contract NNC07CA20C. [1] A. A. Balandin and O. L. Lazarenko, "Mechanism for thermoelectric figure-of-merit enhancement in regimented quantum dot superlattices," *Appl. Phys. Lett.*, 82, 415 (2003). [2] Y. Bao, A. A. Balandin, J. L. Liu and Y.H. Xie, "Experimental investigation of Hall mobility in Ge/Si quantum dot superlattices," *Appl. Phys. Lett.*, 84, 3355 (2004). [3] D. L. Nika, E. P. Pokatilov, Q. Shao and A. A. Balandin, "Charge carrier states and light absorption in the ordered quantum dot superlattices," *Phys. Rev. B*, 76, 125417 (2007). [4] Q. Shao, A. A. Balandin, A. I. Fedoseyev and M. Turowski, "Intermediate-band solar cells based on quantum dot supra-crystals," *Appl. Phys. Lett.*, 91, 163503 (2007).

#### SESSION P3: 3-D Battery Architectures: Materials and Fabrication Methods

Chair: John Thomas

Wednesday Morning, April 15, 2009

Room 2022 (Moscone West)

##### **8:30 AM \*P3.1**

**Electrodeposition as a Versatile Tool for the Fabrication of Three-Dimensional Lithium-Ion Rechargeable Batteries.** Amy Prieto, James Mosby and Timothy Arthur; Chemistry Department, Colorado State University, Fort Collins, Colorado.

The two main limitations to the rate of charging and discharging in Li-ion batteries are the slow diffusion of  $\text{Li}^+$  into the anode and the cathode and the slow diffusion between them. A successful method to decreasing the diffusion length of  $\text{Li}^+$  in intercalation reactions has been to fabricate electrode materials as high surface area nanowire arrays. The fabrication of nanowire arrays of both carbon based anodes and several common cathode materials has been shown to dramatically enhance electrode performance. The problem of decreasing the  $\text{Li}^+$  diffusion length between the cathode and anode has not yet been solved. We are incorporating nanowire arrays of  $\text{Cu}_2\text{Sb}$  anodes into a new battery architecture. Each nanowire anode is conformally coated with a polymer electrolyte via reductive electropolymerization, and then surrounded by the cathode electrode synthesized using sol-gel chemistry. The significant advantage to this geometry is that the diffusion length between the electrodes has been dramatically reduced. Electrodeposition of the anode and the polymer electrolyte is key for the final three-dimensional architecture.

##### **9:00 AM \*P3.2**

**Electrodeposition of Polymer Electrolytes as Battery Separator Layers on Convolved Surfaces.** John Owen<sup>1</sup>, Phil Johns<sup>1</sup>, Matt Lacey<sup>1</sup>, Supputra Visetpotjanakit<sup>1</sup> and Gaber El-Enany<sup>2</sup>; <sup>1</sup>School of Chemistry, University of Southampton, Southampton, United Kingdom; <sup>2</sup>Physics and Math Department, Faculty of Engineering, Suez Canal University, Port Said, Egypt.

Sequential deposition of the three components of a battery onto an arbitrarily shaped surface offers a radical departure from conventional battery fabrication methods. By contrast with the laminate construction, which places a sheet of electrolytic separator in between two electrode-coated foils or plates, the sequential deposition route can, in principle, be applied to a general, convoluted surface such as the inside of a porous metal. From the several methods available for the deposition of electrodes, e.g. electrodeposition of metals and metal oxides, chemical vapour deposition and sol-gel deposition of compounds, electrodeposition has the advantages of self-leveelling and pinhole-filling if the resistance of the product can be made to control the deposition rate. Therefore, electrodeposition is an ideal method for producing the homogeneous, conformal coatings required of the separator layer to encourage a uniform current distribution during battery operation. Electrodeposition of electrolyte separators is relatively novel, and unusual because the separator lacks, by definition, the electronic conductivity normally required for deposition of a layer of non-infinitesimal thickness. This paper will outline examples of two ways in which this apparent impossibility can be circumvented. The first method uses electropolymerization as previously used in corrosion protection of metals. Vinyl polymerization has been achieved through the formation of polymerization initiators by electron transfer from the substrate, followed by diffusion of initiator and reactants through the film. Examples will be given for polyacrylonitrile and oligo-ether substituted vinyl monomers. Surface conductance values of around 10 Ohm cm<sup>2</sup> have been achieved after plasticization of layers up to 10 microns in thickness with added liquid electrolytes. The second method described uses oligoether-substituted pyrrole as the precursor to the growth of an electronically conducting film by electrodeposition. This allows the electrodeposition of an electrode layer on top before finally activating the battery structure by chemically or electrochemically destroying the electron

path through the conjugated structure of the polypyrrole. In this way, complete battery structures can be made entirely by sequential electrodeposition. The presentation will report progress on the application of both methods to planar and 3D substrates and characterization of the electrolyte layers in each case. The initial work was presented at ISPE-11, Ofir, Portugal, Sept 2008. G. M. El Enany†, P. Johns, S. Visetpotjanakit and J. R. Owen\* † on leave from the Department of Physics and Math., Faculty Of Engineering, Suez Canal University, Port Said, Egypt

#### 9:30 AM P3.3

**A High Aspect Ratio Cu<sub>2</sub>Sb Electrode Coated With a Silane-based Polymer Film to be used In a 3D Micro-battery.** Emilie Perre<sup>1,2</sup>, Pierre-Louis Taberna<sup>1</sup>, Torbjorn Gustafsson<sup>2</sup>, Patrice Simon<sup>1</sup> and Kristina Edstrom<sup>2</sup>; <sup>1</sup>Centre Inter-universitaire de Recherche et d'Ingénierie des MATériaux, Université Paul Sabatier, Toulouse, France; <sup>2</sup>Ångström Advanced Battery Centre, Dept of Materials Chem., Uppsala Universitet, Uppsala, Sweden.

Research into energy storage devices is undergoing great changes especially for powering micro/nano applications. New micro battery concepts based on the Li-ion battery technology such as 3-dimensional nano-architecturing are now being explored. The expectation is to maintain the advantage of high kinetics shown by thin-film Li-ion batteries while increasing the energy delivered per foot print area by building a 3D structure. Applicability of the 3D model has already been demonstrated[1] and full or half-cells have been experimentally obtained[2,3,4]. We will present our work on the synthesis of a 3D Li-ion micro battery using chemical/electrochemical methods. Three-dimensionally organised current collectors made of copper or aluminium were grown by direct electrodeposition through an alumina template[4,5], and coated with active material and polymer separator. Such an approach permits the achievement of high aspect ratio columns having diameters below the micrometer range. Herein we present the behaviour of antimony electrodeposited onto copper current collectors, subsequently coated by a polymer separator filled with electrolyte. Sb alloys reversibly with lithium but endeavours high volume variations during the charge/discharge processes. In order to mechanically buffer these changes, alloying of Sb with the copper current collectors has been performed by heat treatment. The addition of a silane-based polymer film onto the so obtained active material will be presented. The obtained cell did not only show an increased capacity per foot print area and a more stable cycling compared to planar systems, but it also maintained its rate capability. 1. Long J. W., Dunn B., Rolison D. R., White H. S. Chemical Reviews 104 (2004) 4463. 2. Golodnitsky D., Yufit V., Nathan M., Shechtman I., Ripenbein T., Strauss E., Menkin S., Peled E. J. Power Sources 153 (2006) 281. 3. Wang C., Taherabadi L., Jia G., Madou M., Yeh Y., Dunn B. Electrochim. Solid-State Lett. 7 (2004) A435. 4. Taberna P. L., Mitra S., Poizot P., Simon P., Tarascon J. M. Nature Mater. 5 (2006) 567. 5. Perre E., Nyholm L., Gustafsson T., Taberna P.-L., Simon P., Edström K. Electrochemistry Communications 10 (2008) 1467.

#### 9:45 AM P3.4

**Nanostructured Anodes for 3D LI-Ion Microbatteries based on Copper Nano-architectured Current Collector** Laurent Bazin, Marie-Joelle Menu and Patrice Simon; CIRIMAT UMR-5085, Université Paul Sabatier, Toulouse Cedex 4, France.

Recent breakthrough in the field of nano-technology will hopefully lead to the replacement of traditional electronic systems by microelectronic devices, designed at the nanoscale. These advances, in association with the increasing need for autonomy in portable device applications dragged the energy storage field toward a new goal: to design battery systems capable to be integrated in micrometric objects. In this optic, 3D microbatteries is a promising approach, based on a clever use of the third dimension of batteries. This strategy has been successfully used in various work [1, 2], leading to high power and energy volumic densities. In this work, we propose nano-architectured electrodes for 3D Li-ion batteries, using electrodeposited Sn as active material. Also, a similar coating was achieved by EPD using SiO<sub>2</sub> particles as model compound. High surface area nano-architectured copper current collectors have been designed based on simple electrodeposition method [3]. It consists in arrays of pure Cu pillars (2μm long, 200 nm diameter). The nano-architectured electrode design not only increases the effective surface area of the electrode but it is also very suitable for sustaining the mechanical and structural stain during electrochemical reaction. It is also providing better electronic and ionic conduction. A nano-architectured Sn anode for Li-ion battery, based on Li-Sn alloying reaction, was prepared by coating this nanostructure by pulsed ELD. It delivers very high cycle life and good power performance compared to planar tin films. This electrode should be successfully used in the field of 3D microbatteries. Following this work, we also achieved a versatile electrophoretic coating of the nano-architectured current collector [4]. Silica nanoparticles were used as a model compound, leading to well covering, thin film on the Cu rods.. The use of this technique open the way for the deposition of a large variety of materials that cannot be deposited by ELD, with controllable cristalinity and particles size. Ref: 1) J.W. Long, B. Dunn, D.R. Rolison, H.S. White, Chem Rev 104 (2004) 4463 2) M. Nathan, D. Golodnitsky, V. Yufit, E. Strauss, T. Ripenstein, I. Shechtman, S. Menkin, E. Peled, Journal of microelectromechanical systems 14 (5) (2005) 879 3) P.L. Taberna; S. Mitra, P. Poizot, P. Simon, J.-M Tarascon, Nature Material, 5 (2006) 567 4) L. Bazin, M. Gressier, P.-L. Taberna , M.-J. Menu, P. Simon, Chem. Commun (2008) 5004

#### 10:30 AM \*P3.5

**Lithium Phosphorous Oxynitride (Lipon) Electrolyte for Rechargeable Batteries with Three-Dimensional Architectures** Nancy J Dudney<sup>1</sup>, Fan Xu<sup>1</sup>, Can Erdonmez<sup>2</sup>, Wei Lai<sup>2</sup> and Yet-Ming Chiang<sup>2</sup>; <sup>1</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The glassy lithium phosphorous oxynitride electrolyte, known as Lipon, has been successfully applied in the development of thin film rechargeable lithium and lithium-ion batteries. The modest lithium ion conductivity, ~2μS/cm, is sufficient for most devices when deposited by RF sputtering as thin films with a thickness of ~1μm. The stability of the Lipon films allows for high voltage lithium batteries, high temperature processing, and exposure to air during battery fabrication. In addition, the Lipon has a high

electronic resistivity that prevents self-discharge. Recent work is exploring whether Lipon can be used as an electrolyte for some of the more complex 3D architectures being investigated for solid state batteries. Using a planar magnetron sputtering source and nitrogen process gas, the composition, morphology, and conductivity of the film has been characterized for surfaces positioned at grazing angles and at angles completely shadowed from the line-of-sight to the magnetron source. Although the film composition varied, a dense morphology and good lithium ion conductivity were achieved. In addition, Lipon coverage has been evaluated for several different surfaces with regular 10-100  $\mu\text{m}$  features, including porous membranes and arrays of posts. Acknowledgement: This work was supported by DARPA Defense Sciences Office and by the Division of Materials Sciences and Engineering, U.S. Department of Energy.

#### 11:00 AM P3.6

**Microporous vs. Planar Intermetallic Anodes for Li-Ion Batteries.** Lynn Trahey<sup>1,2</sup>, John T Vaughney<sup>1</sup>, Harold H Kung<sup>2</sup> and Michael M Thackeray<sup>1</sup>; <sup>1</sup>Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Chemical and Biological Engineering, Northwestern University, Evanston, Illinois.

The future of lithium-ion batteries, the staple of portable energy storage, relies on improving the anode in terms of safety and energy. Most state-of-the-art batteries use graphitic carbon, although alternative materials such as Sn-based compounds and Si are being advocated because they offer larger volumetric and gravimetric capacities. In general, the drawback of Sn-based and Si materials is that they tend to disintegrate on cycling as a result of the large volume changes incurred on cycling, which leads to short electrode lifetimes. By using intermetallic compounds that show strong structural relationships before and after reaction with lithium, such as Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>2</sub>Sb, the volume expansion is lowered significantly and the cycle life improved; however, further improvements in electrochemical performance of these anode materials are still required [1]. In efforts to enhance the electrochemical properties of Cu-based intermetallic electrodes, we have adopted an approach using electrodeposition techniques to engineer 3-D porous copper foam current collecting architectures with sufficient void volume to accommodate the expansion of the active electrode particles; our recent work on Sn-Cu<sub>6</sub>Sn<sub>5</sub> anodes has led to promising results [2]. In order to raise the average operating potential of the anode, we have extended this work to composite Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>2</sub>Sb electrode systems. Thin film (2-D) and microporous (3-D) architectures, synthesized by direct and pulsed electrodeposition, have been explored. Electrodes were analyzed by scanning electron microscopy, energy dispersive spectrometry and powder X-ray diffraction before and after electrochemical coin cell cycling to assess the changes in electrode morphology, composition and crystallinity. The effects of Cu-foam sintering and active material annealing, as well as key differences in electrode stability and cycling kinetics between 2-D and 3-D architectures will be discussed. Acknowledgments Financial support from the Office of Vehicle Technologies of the U.S. Department of Energy under Contract DE-AC02-06CH11357 and Center for Energy Efficient Transportation at Northwestern University is gratefully acknowledged. References [1] M. M. Thackeray, J. T. Vaughney, C. S. Johnson, A. J. Kropf, R. Benedek, L. M. L. Fransson, K. Edstrom, *Journal of Power Sources*, 113 (2003) 124-130. [2] L. Trahey, J. T. Vaughney, H. H. Kung, M. M. Thackeray, *Electrochem. Comm.* (2008). Submitted.

#### 11:15 AM P3.7

**Metal-Oxides-Coated LiCoO<sub>2</sub> with Atomic Layer Deposition for All-Solid-State Lithium Secondary Batteries** Yoon Seok Jung<sup>1</sup>, James Trevey<sup>1</sup>, Andrew S. Cavanagh<sup>2</sup>, Markus D. Groner<sup>2</sup>, Steven M. George<sup>2</sup> and Sehee Lee<sup>1</sup>; <sup>1</sup>Mechanical Engineering, University of Colorado at Boulder, Boulder, Colorado; <sup>2</sup>Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Colorado.

<p align="justify">Lithium ion batteries (LIBs) using liquid electrolyte have been widely used in various portable electronic devices. Even further, their development for hybrid electric vehicles (HEV) is a current focus. However, current LIBs suffer from intrinsic safety problem concerning flammable liquid electrolyte. In this regard, all-solid-state Li secondary batteries can be the ultimate solution for the safety issue. As sulfide-based superionic electrolytes which represent high conductivity ( $10^{-4}\text{--}10^{-3}$  S cm<sup>-1</sup>) at room temperature close to that of liquid electrolyte ( $10^{-3}\text{--}10^{-2}$  S cm<sup>-1</sup>) have been developed, all-solid-state "composite" batteries which may even compete with current LIBs on the aspect of high capacity have been studied.[1,2] In spite of high capacity achieved by this "composite" configuration, the rate capability of all-solid-state lithium secondary batteries is generally very poor. Takada group reported that the high interfacial resistance between active powders and solid electrolyte (SE) is the origin of still low power density even when high-conductivity SE is used.[3] And it was reported that the high interfacial resistance can be dramatically reduced by coating electrically insulating metal-oxide layer on the active powders.[3] Recently we have developed an atomic layer deposition (ALD) process for the metal-oxide coating on electrode materials for all-solid-state lithium secondary batteries. Compared with the sol-gel method which requires an excess amount of precursors, solvent, and post-heat-treatment process, and etc, ALD is much more cost-effective. Furthermore, precise control of atomic scale coating thicknesses and almost 100% surface coverage contribute to the outstanding advantages of ALD.[4] Various metal oxides including Al<sub>2</sub>O<sub>3</sub> were coated on the LiCoO<sub>2</sub> by ALD and with controlled coating thicknesses from ~0.2 to ~20 nm. Using xLi<sub>2</sub>S-(100-x)P<sub>2</sub>S<sub>5</sub> (x = 70-80) glass prepared by mechanical milling as SE, all-solid-state cells In / SE / coated LiCoO<sub>2</sub> were fabricated. Compared with bare LiCoO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> represents higher reversible capacity when cycled with 75  $\mu\text{A cm}^{-2}$  in the potential range of 2.5-4.3 V (vs. Li/Li<sup>+</sup>) at 50°C. First discharge capacity is 60 mA h g<sup>-1</sup> and 100 mA h g<sup>-1</sup> for bare LiCoO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub>, respectively. This could be attributed to the decreased interfacial resistance by introducing Al<sub>2</sub>O<sub>3</sub> layer between SE and LiCoO<sub>2</sub>. The electrochemical response of LiCoO<sub>2</sub> varied by metal oxide species and thickness of layers will be discussed in detail, wherein major focus will be paid on the interfacial kinetics. References [1] F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Adv. Mater.*, **17**, 918 (2005). [2] M. Tatsumisago, F. Mizuno, A. Hayashi, *J. Power Sources*, **159**, 193 (2006). [3] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, *Adv. Mater.*, **18**, 2226 (2006). [4] S. M. George, A. W. Ott, J. W. Klaus, *J. Phys. Chem.*, **100**, 13121 (1996).

**11:30 AM P3.8**

**Microstructure Design of Portable Power Sources through Finite Element Analysis.** Madeleine Smith and R. Edwin Garcia; Materials Engineering, Purdue University, West Lafayette, Indiana.

Economical and practical considerations for new technologies result in an increase of demand for electrical power sources with higher energy and power densities than those currently available. As a result, crucial material challenges arise, and material non-idealities, conceived chemistries, and inherent ohmic losses have motivated the development of new scientific methodologies and out-of-the box engineering approaches to create advanced power sources. The present paper presents a theoretical and numerical framework that spatially resolves the thermodynamic and kinetic properties of the constituent materials of rechargeable lithium ion batteries microstructures. For traditional topologies, bottleneck microstructural mechanisms and limiting rates are identified. Improved traditional and three-dimensional architectures are proposed, and the location of undesirable microstructural features are identified for real and computer-generated electrode architectures.

**11:45 AM P3.9**

**Aligned Carbon Nanotubes for Nanostructured Lithium-Ion Battery Electrodes** Daniel Welna<sup>1,2</sup>, Barney Taylor<sup>1,2</sup>, Liangti Qu<sup>3</sup>, Liming Dai<sup>3</sup> and Michael Durstock<sup>1</sup>; <sup>1</sup>Air Force Research Laboratory, Wright-Patterson AFB, Ohio; <sup>2</sup>Universal Technology Corporation, Dayton, Ohio; <sup>3</sup>Department of Chemical and Materials Engineering, University of Dayton, Dayton, Ohio.

Nanostructured electrodes offer an exciting solution to current battery technology limitations related to their size and power to weight ratio. Their increased surface area allows for two fundamental improvements over conventional flat electrode designs: 1) higher lithium uptake leading to increased storage capacity and 2) increased rate capability allowed through faster interfacial kinetics. Although nanostructured electrodes can lead to significantly increased performance, there is a need to understand how the nanoscale morphology affects electrochemical behavior. This work focuses on understanding the relationship between electrochemical behavior (capacity, cyclability, and rate capability) and nanoscale morphological control of lithium-ion battery electrode materials, specifically analyzing carbon-based electrode materials. The current state-of-the-art of lithium-ion batteries utilizes graphite as a negative electrode with a maximum theoretical specific capacity of 372 mAh/g and a practical specific capacity ranging from 150-370 mAh/g [1]. Vertically-aligned multi-walled carbon nanotube (VAMWNT) electrodes, which were aligned in the direction of current flow, were examined in this work. By aligning the nanotubes in this manner, increased access and interfacial dynamics between lithium-ions and the interstitial spaces of the MWNTs as well as the internal and external surfaces of the MWNTs were allowed. These electrodes were able to produce a stable and reversible capacity of 650 mAh/g. Excellent rate capability was also shown as the VAMWNTs were able to achieve 500 mAh/g at a discharge rate of ~400 mA/g (1.3C). Furthermore, moderate specific capacities were obtained at very high discharge rates. X-ray diffraction and Raman spectroscopy were utilized to provide a means of relating the electrode performance characteristics to the morphological changes occurring during the lithium-ion insertion and de-insertion process. 1. Linden, D.; Reddy, T.B., *Handbook of Batteries*, 3rd ed. McGraw-Hill Co., Inc.: New York, 2005.

**SESSION P4: Solar Cells with 3D Architectures**

Chairs: John Rogers and Yang Yang  
Wednesday Afternoon, April 15, 2009  
Room 2022 (Moscone West)

**1:30 PM \*P4.1**

**Si Wire Array Solar Cells** Harry A. Atwater, Nathan S Lewis, Michael D Kelzenberg, Morgan C Putnam, Joshua M Spurgeon, Daniel B Turner-Evans and Jan A Petykiewicz; Applied Physics, California Institute of Technology, Pasadena, California.

Silicon wire array solar cells are three dimensional photovoltaic absorbers which enable orthogonalization of light absorption and carrier collection in dense arrays of high aspect ratio micron-scale wires, enabling efficient collection even in relatively impure silicon material characterized by micron-scale minority carrier diffusion lengths. Silicon wire arrays are grown by vapor-liquid-solid growth on a lithographically patterned array of catalyst particles. Following growth on a crystalline (111) Si wafer, Si wire arrays are embedded in a polymethylsiloxane (PDMS) film and can be peeled off the growth template substrate, yielding an unusual photovoltaic material: a flexible, bendable, wafer-thickness Si absorber. Following wire array peel off, the original growth template substrate can be reused for subsequent array growth without further lithography. In this paper, I will describe the observation of enhanced absorption in wire arrays relative to planar Si cells of equivalent material thickness as well as photovoltaic cell results obtained to date and directions for future cell processes and designs.

**2:00 PM P4.2**

**Solution Processed Cu<sub>2</sub>O/ZnO Nanowire Solar Cell.** John H Joo<sup>1</sup>, Jacob J Richardson<sup>1</sup>, Frederick F Lange<sup>1,2</sup> and Evelyn L Hu<sup>1,3</sup>; <sup>1</sup>Materials Department, University of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California; <sup>3</sup>Department of Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California.

The integration of nanostructured materials in solar cell design offers new opportunities for device optimization. The planar solar cell structure has been the conventional structure; but the needs for both large area photon collection and efficient carrier collection provide a challenge to device performance, even when the absorption length and the minority carrier diffusion length of the semiconductor are similar in magnitude. This situation is aggravated for materials with short minority carrier diffusion lengths.

Solar cell structures based on vertically aligned arrays of semiconductor nanowires do not require the minority carrier diffusion length to be as large as the absorption length, because they separate the absorption direction from the carrier collection direction. Consequently, the nanowire structure provides a natural means of device optimization and opens the possibility of using low cost semiconductors not traditionally used in solar cells. We report on the fabrication and characterization of a solar cell created by electrodepositing Cu<sub>2</sub>O on an array of ZnO nanowires grown in water at 90°C. The aqueously grown ZnO is n-type with a band gap of 3.4 eV and serves as the window layer; the electrodeposited Cu<sub>2</sub>O is p-type with a smaller band gap of 2.0 eV and serves as the absorber layer. The bottom up growth of the ZnO nanowire array eliminates the need for templates or lithography, keeping the process simple and inexpensive. We examine the growth of Cu<sub>2</sub>O on the nanostructured ZnO and show complete filling and planarization of the ZnO nanowire array. I-V measurements of these devices are compared to similar devices made using planar ZnO. Initial results indicate V<sub>oc</sub> of 0.13 V, J<sub>sc</sub> of 1.1 mA/cm<sup>2</sup>, and FF of 43% for the nanostructured device tested using an Oriel solar simulator with Xe lamp. These results demonstrate a pathway toward low cost solar cells.

#### 2:15 PM P4.3

**Quantum Dot Sensitized TiO<sub>2</sub> Nanotube Solar Cells.** Jun Wang, Jun Xu and Zhiqun Lin; Department of Materials Science and Engineering, Iowa State University, Ames, Iowa.

We report the rational design and engineering of quantum dot sensitized nanostructured solar cells (QDSNSC) by infiltrating quantum dots (e.g., CdSe QDs) into highly ordered anodic TiO<sub>2</sub> nanotubes. A water soluble bifunctional group (i.e., dithiocarbamate) capped CdSe QDs was synthesized via a biphasic ligand exchange. The -COOH group at the dithiocarbamate-functionalized CdSe QDs surface reacts with the -OH group at the TiO<sub>2</sub> nanotubes surface, thereby facilitating electronic interaction between the electron donor (i.e., CdSe) and electron accepter (i.e., TiO<sub>2</sub>). Oxygen plasma treatment was carried out on the TiO<sub>2</sub> nanotubes for improving coverage of CdSe quantum dots by saturating the -OH group on the TiO<sub>2</sub> nanotube walls. The effects of the size of CdSe QDs, the aspect ratio of TiO<sub>2</sub> nanotubes, and the oxygen plasma treatment on the performance of resulting QDSNSC were studied.

#### 2:30 PM P4.4

**Vertical Phase Separation In Poly(3-hexylthiophene):Fullerene Derivative Blends and Its Advantage for Inverted Structure Solar Cells.** Li-Min Chen<sup>1</sup>, Zheng Xu<sup>1</sup>, Guanwen Yang<sup>1</sup>, Jianhui Hou<sup>2</sup>, Yue Wu<sup>2</sup>, Gang Li<sup>2</sup> and Yang Yang<sup>1</sup>;

<sup>1</sup>Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California; <sup>2</sup>Solarmer Energy Inc., El Monte, California.

We utilized a unique method, using water to lift-off the polymer blend films to investigate the buried polymer/substrate interface without altering the film properties. The PCBM/P3HT ratios were evaluated using carbon/sulfur (C/S) atomic ratios obtained from XPS analysis, which revealed spontaneous vertical phase separation upon spin-coating, as well as enrichment of the donor and acceptor components at the top and bottom surfaces, respectively. This vertical phase separation is attributed to the surface energy differences of P3HT and PCBM, as well as induced dipole-dipole interactions between PCBM and the substrates. This inhomogeneous phase distribution, with P3HT-rich layer at the metal electrode and PCBM-rich at the ITO side is contrary to the ideal morphology for the regular device structure; however, polymer films with this vertical phase separated morphology are beneficial for charge collection in the inverted configuration. By varying the substrate surface property, the distribution of the donor and acceptor materials can be manipulated, and the PCBM concentrations at the polymer/Cs<sub>2</sub>CO<sub>3</sub> interfaces are higher than at the polymer/glass or polymer/PEDOT interfaces, indicating enhanced vertical segregation on Cs<sub>2</sub>CO<sub>3</sub>-coated ITO substrates. Our work unveiled the advantage of the inverted configuration, validated by the I-V characteristics and EQE results, with 4.2% PCE and EQE maximum at 72%. This device performance is comparable to the regular structure based on the same system, and provides a promising alternative for structure design flexibility in tandem cell application.

#### 2:45 PM P4.5

**Three-Dimensionally Configured Dye-Sensitized Solar Cells.** Cyrus Rustomji<sup>1,2</sup>, Christine Cobb<sup>2</sup>, Michael Tauber<sup>1,2</sup> and

Sungho Jin<sup>2</sup>; <sup>1</sup>Chemistry and Biochemistry, University of California at San Diego, San Diego, California; <sup>2</sup>Materials Science and Engineering, University of California at San Diego, La Jolla, California.

Dye sensitized solar cells (DSSC) based on a mesoporous TiO<sub>2</sub> titanium dioxide nanoparticle layer and ruthenium sensitizers have been the subject of intense research as an alternative to traditional solid-state cells. Modest increases in efficiency have been demonstrated in recent years, however the open circuit voltage (~0.7 V), short circuit current (~20mA/cm<sup>2</sup>), fill-factor (~0.70) and overall efficiency (~11%)[1] of the best DSSC's are all significantly below desired values in standard AM 1.5 solar conditions. Our research focuses on a new cell that is based upon ~10 micrometer long and 100 nm diameter TiO<sub>2</sub> nanotubes that are arranged in a three-dimensional architecture, exhibiting orders of magnitude larger surface reaction area. Unlike prior designs that utilize vertically aligned tubes[2,3], our cell is comprised of nanotubes that are arranged radially from a grid of fine titanium wires. The tubes and Ti metal substrate to which the nanotubes have solid contacts provide a direct and low-resistance conduit for capture of electrons at the anode, while still maintaining very high surface area for covalently binding inorganic or organic sensitizers. Light can be effectively absorbed by our cell, even into the near-IR region, because the path-length of the TiO<sub>2</sub> nanotube layer is significantly greater than the thickness of the mesoporous TiO<sub>2</sub> layer of traditional DSSCs. Furthermore, the new architecture does not require any transparent conductive glass at either electrode, which results in an increase in efficiency and simplification of our cell that is not possible in the traditional design. Based on our preliminary measurements and estimations, it is anticipated that the nanotube 3-D architecture explored in our work, especially with multilayered or hierarchically vertical arrayed configurations, will lead to cell efficiencies that will exceed the current record of 11% that has been demonstrated

for the best DSSC to date. [1] Mohammad K. Nazeeruddin, Michael Gratzel, J Am. Chem Soc. 2001, 123: 1613-1624 [2] Karthik Shankar, Gopal K Mor, Haripriya E Prakasam, Craig A Grimes, Nanotechnology 2007, 18, 065707 [3] Kai Zhu, Nathan R Neale, Alexander Miedaner, Arthur J Frank, Nano Letters, 2007, v.7, 1, 69-74

3:30 PM \*P4.6

Silicon Microcell Photovoltaics John Rogers, University of Illinois, Urbana, Illinois.

Silicon, in amorphous or various crystalline forms, is used in >90% of all installed photovoltaic (PV) capacity. The high natural abundance of silicon, together with the excellent reliability and good efficiency of solar cells made with it suggest its continued use, on massive scales, for the foreseeable future. In this talk, we describe the use of this relatively old material in the form of micro-cells created from bulk wafers and integrated in diverse spatial layouts on foreign substrates by transfer printing. The resulting devices can offer useful features, including high degrees of mechanical flexibility, user-definable levels of transparency and ultra-low profile micro-optic concentrator designs. Detailed studies of the processes for creating and manipulating such micro-cells, together with investigations of the electrical, mechanical and optical characteristics of several types of modules that incorporate them illuminate the key aspects. The results represent strategies that might expand the application possibilities for monocrystalline silicon PV.

4:00 PM P4.7

Improved Short-Circuit Current in Hybrid Photovoltaics by Lithium Doping of Zinc Oxide. Matthew Thomas Lloyd, Yun-ju Lee and Julia W Hsu; Surface and Interface Sciences, Sandia National Laboratories, Albuquerque, New Mexico.

While ZnO/polymer heterojunctions offer a route to low temperature, solution processed nanostructured photovoltaics, these devices typically suffer from very low efficiencies stemming from low short-circuit current ( $J_{sc}$ ). Typically, hybrid devices utilize ZnO films or nanorod arrays that are not intentionally doped. Consequently, there is no control over the conductivity or the position of the Fermi-energy level in ZnO. By loading sol-gel derived ZnO films with 5% (atomic) lithium, we observe a 45% increase in  $J_{sc}$  compared to undoped ZnO/poly-3-hexylthiophene (P3HT) photovoltaic devices. Kelvin probe results show a monotonic decrease in the work function of ZnO as a function of lithium concentration. This suggests that the role of lithium might be to decrease the barrier to charge extraction between the ZnO electron acceptor layer and the ITO electrode, leading to increased photocurrent. We also investigate the relative position of a thin lithium doped layer within the device architecture. Compared to undoped ZnO/P3HT, we a significant increase in efficiency when the ZnO/polymer interface is doped with lithium; however, the improvement is even greater when the ITO/ZnO interface is doped with lithium. To further understand the origin of the performance enhancement, we characterize the chemical and electrical properties of lithium doping in thin films of ZnO. Experiments are also underway to extend lithium doping to 3D nanostructured solar cells. Preliminary results suggest that the performance of ZnO nanorod based devices is enhanced when the ITO and ZnO seed layer interface is doped with lithium. Incorporation of lithium doped ZnO nanorods as the electron acceptor will also be investigated. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15 PM P4.8

Wafer-scale Photovoltaic Application of Radial p-n Junction Silicon Nanowire Arrays Prepared by Metal-induced Electroless Etching with Plasma Conformal Doping. Jin-Young Jung<sup>1</sup>, Sang-Won Jee<sup>1</sup>, Han-Don Um<sup>1</sup>, Jong-Yeoul Ji<sup>2</sup>, Chung-Tae Kim<sup>2</sup> and Jung-Ho Lee<sup>1</sup>; <sup>1</sup>Chemical Engineering, Hanyang University, Ansan, Kyunggi, Korea, South; <sup>2</sup>ADP engineering CO., LTP, Seongnam, Korea, South.

Silicon nanowire (SiNW)-based solar cells offer new opportunities for addressing the efficiency and cost issues of photovoltaic since one-dimensional (1D) nanowires with a p-n junction in a radial direction can allow for separation of light absorption and carrier extraction into two orthogonal directions, thus giving rise to high efficiency. Since SiNWs of controlled properties, such as diameters, electronic properties, crystallographic orientation and location, are needed for solar cell application, much effort has been devoted to the fabrication of SiNWs by various techniques. In general, the bottom-up method for synthesis of SiNWs is vapor-liquid-solid (VLS) growth using Au as catalysts, because the Au-catalyzed-grown SiNWs have a superior crystalline morphology and good controllability. But VLS growth method is not easy to control the doping gradient and crystallographic orientation. Here, we report the fabrication of wafer-scale arrays of p-type SiNWs directly from heavily doped silicon wafers prepared by metal-induced electroless etching, and then n-type ultra-shallow junction can be formed by using plasma ion doping for making a radial p-n junction of nanowire solar cells. Metal-induced etching has the several advantages of simplicity, low-cost, wafer-scale fabrication of SiNWs without the need of doping. However, it is difficult to control over a wire diameter and spacing due to random distribution of metal. To overcome this hurdle, we have developed the metal-induced etching combined with nanopatterning techniques such as block copolymer assembly and anodic aluminum oxide (AAO) template which can be successfully applied for fabrication of vertically aligned SiNWs. Then, we have investigated the electrical characteristics and a junction depth of ultra-shallow junctions conformally formed by plasma doping inside the SiNWs surface. Phosphine (PH<sub>3</sub>) plasma ion doping process is used to convert the p+ doped SiNWs surface to the n+ SiNWs surface. Electron holography and scanning capacitance microscopy (SCM) were adopted to obtain two-dimensional doping profile of radial p-n junction SiNWs.

4:30 PM P4.9

Silicon Nanowires on Glass Catalyzed by Gold Colloids for Thin Film Solar Cells: Growth, Materials Integration and Characterization. Gerald Broenstrup<sup>1</sup>, Vladimir Sivakov<sup>1</sup>, Thomas Stelzner<sup>1</sup>, Samuel Hoffmann<sup>3</sup>, Christoph Niederberger<sup>3</sup>, Johann Michler<sup>3</sup> and Silke Christiansen<sup>1,2</sup>; <sup>1</sup>Institute of Photonic Technology, Jena, Germany; <sup>2</sup>Max-Planck-Institute of

Microstructure Physics, Halle, Germany; <sup>3</sup>Empa - Swiss Federal Laboratories for Materials Testing and Research, Thun, Switzerland.

Making use of silicon nanowires (SiNWs) in solar cells essentially requires their integration onto cheap glass substrates. This is realized by bottom-up gold nanoparticle (colloids between 10nm and 250nm or droplets from annealing thin gold layers) catalyzed vapour-liquid-solid (VLS) growth of SiNWs from silane by chemical vapour deposition (CVD) at glass compatible temperatures (<600°C). The SiNWs grow in different directions on the glass substrate favouring, but not exclusively, low index growth directions (preferably <111>, <110>, <112>) as determined by electron backscatter diffraction (EBSD) measurements in a scanning electron microscope (SEM). Optical characterization of SiNW carpets grown with different gold colloids using a UV-vis/NIR spectrometer equipped with an integrating sphere suggests that the highest absorption occurs for large SiNW diameters. Passivation of SiNW surfaces is successfully carried out by atomic layer deposition (ALD) of aluminium oxide. Furthermore, passivation and contact formation using transparent conductive oxide is tested by ALD of doped ZnO:Al layers. Axial and radial SiNW doping strategies using co-doping during CVD, ion implantation and thermal activation of dopants as well as dopant diffusion from highly doped spin-on suspensions will be presented, and I-V-measurements will be carried out for single SiNWs in a scanning electron microscope (SEM) and for SiNW ensembles in a probe station. First NW solar cell parameters of contacted SiNW ensembles as well as of single SiNWs will be presented. Additional characterization of structural properties of these SiNWs is carried out using transmission electron microscopy.

#### **4:45 PM P4.10**

**Crystalline-amorphous Si Core-shell Nanowires for Energy Storage.** Li-Feng Cui<sup>1</sup>, Riccardo Ruffo<sup>2</sup>, Candace K Chan<sup>3</sup>, Hailin Peng<sup>1</sup> and Yi Cui<sup>1</sup>; <sup>1</sup>Materials Science & Engineering, Stanford University, Stanford, California; <sup>2</sup>Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, Milan, Italy; <sup>3</sup>Department of Chemistry, Stanford University, Stanford, California.

Silicon is an attractive alloy-type anode material for lithium ion batteries because of its highest known capacity (4,200 mAh/g). However silicon's large volume change upon lithium insertion and extraction, which causes pulverization and capacity fading, has limited its applications. Designing nanoscale hierarchical structures is a novel approach to address the issues associated with the large volume change. In this letter we introduce a core-shell design of silicon nanowires for high power and long life lithium battery electrodes. Silicon crystalline-amorphous core-shell nanowires were grown directly on stainless steel current collectors by a simple one-step synthesis. Amorphous Si shells instead of crystalline Si cores can be selected to be electrochemically active due to the difference of their lithiation potentials. Therefore, crystalline Si cores function as a stable mechanical support and an efficient electrical conducting pathway while amorphous shells store Li ions. We demonstrate here that these core-shell nanowires have high charge storage capacity (~1000 mAh/g, 3 times of carbon) with ~90% capacity retention over 100 cycles. They also show excellent electrochemical performance at high current charging and discharging (6.8 A/g, ~20 times of carbon at 1 hour rate).

**SESSION P5: Poster Session**  
**Wednesday Evening, April 15, 2009**  
**8:00 PM**  
**Salon Level (Marriott)**

#### **P5.1**

**Macroporous 3D Architectures of Self-Assembled MWCNTs Surface as Anodes for Fuel Cells.** Francisco del Monte<sup>1</sup>, Maria C. Gutierrez<sup>1</sup>, Maria J. Hortiguela<sup>1</sup>, Ricardo Jimenez<sup>1</sup>, J. Manuel Amarilla<sup>1</sup>, Luis Yuste<sup>2</sup>, Fernando Rojo<sup>2</sup> and Maria L. Ferrer<sup>1</sup>; <sup>1</sup>ICMM-CSIC, Madrid, Spain; <sup>2</sup>CNB-CSIC, Madrid, Spain.

Microchannelled 3D architectures composed of multiwall carbon nanotubes (MWCNTs) surface decorated with Pt nanoparticles and chitosan (CHI) are prepared by ice segregation induce self assembly (ISISA) process. The ISISA process consists on the unidirectional freezing (at -196 degrees C) of the hydrogel nanocomposites. Upon freezing, the ice formation (hexagonal form) causes every solute originally dispersed in the hydrogel to be segregated from the ice phase. After freeze-drying, the resulting hierarchical structures consists on well aligned micrometer-sized pores in the freezing direction corresponding to the empty areas where ice crystals originally resided, being the macrostructure supported by the matter accumulated between adjacent ice crystals. For high MWCNTs contents (89 wt. %), the resulting architectures are highly porous (specific gravity ~9.4 10-2) and extremely conductive (2.5 S cm-1) thanks to the MWCNT interconnection at the macrostructure. These macroporous 3D architectures offer a high internal reactive surface of easy access through the broad "highways" provided by the microchannelled structure, which make them highly suitable for catalytic purposes. In particular, the Pt/MWCNTs(89)/CHI 3D architectures (prepared from Pt surface decorated MWCNTs) have allowed for a remarkable improvement (e.g., current densities of up to 242 mA cm-2) of the catalytic activity toward the methanol oxidation thanks to efficient fuel and product diffusion. Moreover, attempts for bacteria immobilization within the 3D structure are currently under progress with the aim of preparation of a microbial fuel cell (MFC).

#### **P5.2**

**Microstructural and Chemical Characterizations of Anodes of LSCrRuO Fuel Cells** Yougui Liao, David Bierschenk, Scott Barnett and Laurence Marks; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Y. Liao, D. Bierschenk, S. Barnett, L. Marks Department of Materials Science and Engineering MSE Rm 2036 Cook Hall 2220 N

Campus Drive Northwestern University Evanston, IL 60208, USA Many efforts are presently directed to develop micro solid oxide fuel cells (SOFCs) because they are fundamentally applicable to power generation in stationary, portable and transport applications and potentially satisfy our increasing need for sustainable energy resources. The key feature of a fuel cell is its high energy conversion efficiency. However, the reliability and stability of the SOFCs, operating in high temperature conditions, are still a question. Thus, the understanding of degradation sources and mechanisms is very important for the development of reliable SOFCs. Study of SOFCs, containing anodes consisting of  $\text{La}_{x}\text{Sr}_{1-x}\text{Cr}_{1-y}\text{Ru}_{y}\text{O}_{3-\delta}$  (LSCrRu) and  $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  (GDC), and  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM) electrolytes, is presented here. The samples are analyzed by scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with Energy Dispersive X-ray (EDX) and Electron Energy Loss Spectroscopy (EELS) for compositional analysis. Two different experiments were carried out during this study: 1) TEM measurements on LSCrRu powders; 2) SEM and TEM measurements on actual fuel cells. The powders analyzed are formed at various annealing temperatures and times in a tube furnace with a gas flow of H<sub>2</sub> humidified with 3% H<sub>2</sub>O, similar to that used during SOFC testing and operated fuel cells. A dual-beam focused ion beam - scanning electron microscopy (FIB-SEM) has been used to etch the actual fuel cells for the analyses. Those SEM and TEM sample preparations of complex fuel-cell anode structures yielded an accurate localization of the cells and enabled correct investigation of the properties of anodes and interfaces between anodes and electrolytes. TEM reveals Ru nano-particles on LSCrRu surfaces of annealed materials and some actual fuel cells and, Ru surface coverage. EDX and EELS reveals interdiffusion phenomena between anodes and electrolytes.

**P5.3****Abstract Withdrawn****P5.4****Abstract Withdrawn****P5.5**

**Expanded 3D Electrode Architecture for Low Temperature Direct Liquid Fuel Cells.** Richard Craig Urian, Code 8231, Naval Undersea Warfare Center, Newport, Rhode Island.

The US Navy continues to pursue electrochemical power sources with high energy density for low rate, long endurance undersea applications. The direct electro-oxidation and electro-reduction of sodium borohydride and hydrogen peroxide are being investigated to meet these goals. In an effort to minimize polarization losses and increase power density, a novel carbon microfiber array (CMA) electrode in combination with a carbon cloth electrode is being investigated. The CMA is composed of 750 micron long, 10 micron diameter graphite fibers that protrude from a current collector like blades of grass. The CMA was developed for the direct reaction of peroxide in the Mg-H<sub>2</sub>O<sub>2</sub> semi fuel cell. [1] There, the high surface area of the microfiber cathode reduces peroxide concentration polarization, resulting in increased power and energy density. For this work the CMA architecture was adapted into a novel membrane electrode assembly and evaluated in the direct BH<sub>4</sub>- / H<sub>2</sub>O<sub>2</sub> fuel cell. The unique feature of this architecture vs. traditional membrane electrode assemblies (MEAs) is how all three components of the triple boundary interface are optimized: electrical connectivity, ionic connectivity and mass transport. Half cell polarization measurements were obtained simultaneously with the fuel cell polarization. Initial results using this modified CMFA electrode architecture show that the polarization losses observed for both the reduction of hydrogen peroxide and for the oxidation of borohydride were 5.2 times lower than for the non-modified CMAs electrode (0.014 ohms vs. 0.074 ohms). Comparing these results to those calculated from the literature, [2, 3] 5 and 2.6 times improvements were obtained (0.07 ohms and 0.037 ohms were the effective resistive losses seen in the anode half cell polarizations). Efforts continue to optimize the improvements made thus far and to investigate other catalysts that may not have the same activity as those currently being used in the direct BH<sub>4</sub>- / H<sub>2</sub>O<sub>2</sub> but could improve the operating voltage and electrochemical conversion efficiencies of the fuel and oxidant. References 1. C. Patrissi, R. Bessette, Y. Kim, C. Schumacher, J. Electrochem. Soc., 155, B558 (2008). 2. C. Ponce de Leon, F. Walsh, C. Patrissi, M. Medeiros, R. Bessette, R. Reeve, J. Lakeman, A. Rose, D. Browning, Electrochem. Commun. 10, 1610 (2008). 3. R. K. Raman, S. K. Prashant, A. K. Shukla, J. Power Sources, 162, 1073 (2006).

**P5.6****Abstract Withdrawn****P5.7****Abstract Withdrawn****P5.8**

**Novel Single-chamber SOFC with Superlattice Composite Electrolytes** Zhilang Xu<sup>1</sup>, Man Yang<sup>2</sup>, D. Kumar<sup>1</sup>, S. Desai<sup>2</sup> and Jag Sankar<sup>1</sup>; <sup>1</sup>Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina; <sup>2</sup>Industrial Engineering, North Carolina A&T State University, Greensboro, North Carolina.

Recent research revealed that the electrical conductivity of thin film composite electrolytes was significantly enhanced when the thickness of each sandwiched layer was less than 60 nm. It is attributed to a nanoscale effect in the interfaces with exceptional high ionic conductivity. However, the exceptional ionic conductivity is only available in the plane of the films, while the conductivity in the direction normal to the films is zero if one of the composite layers is nonconductive to ions. Therefore, it is not useful in the solid oxide fuel cells with the traditional structures. To take advantages of the outstanding in-plane conductivity of the superlattice

composite electrolyte, the authors of this presentation have developed a novel single chamber in-plane SOFC by photolithography and physical vapor deposition. In this study, nanostructure superlattice composite electrolytes of  $\text{CeO}_2$ -Sc-doped  $\text{ZrO}_2$  (Ce-SSZ) and  $\text{Al}_2\text{O}_3$  were prepared with pulsed laser deposition (PLD) in the patterns that were created with lithography method. The electrodes at the both sides of the electrolyte were also produced by lithography and PLD. The effects of the layer thickness of the composite electrolytes as well as its width on the conductivity were investigated with ac impedance in comparing to monolithic SSZ electrolytes. Fuel cells with inter-digitized structure of electrolytes and electrodes have been developed and tested. The study showed a great potential of this novel type of fuel cell in the future applications.

#### **P5.9**

**Three Dimensional Electrodes for Increased Performance In Flowing Electrolytes.** Christian Robert Schumacher and Charles J Patrissi; Naval Undersea Warfare Center (NUWC), Newport, Rhode Island.

A fabrication process and performance data for a novel microporous electrode, called the Carbon Microfiber Array (CMA) is presented. This electrode showed significant improvement in concentration polarization characteristics over a conventional planar cathode in the ONR-sponsored Mg-H<sub>2</sub>O<sub>2</sub> semi fuel cell (SFC). Preliminary investigation of structure/processing parameters, are presented in an effort to develop an optimized architecture for a given flow regime or application. Linear sweep (LSV) and cyclic voltammogram (CV) kinetic studies were performed in quiescent and rotating disc electrode (RDE) experiments.

#### **P5.10**

**Lateral Growth of Deep Nanopores In Anodic Aluminum Oxide as a Platform for Energy Nanodevices.** Israel Perez<sup>1</sup>, Parag Banerjee<sup>1</sup>, Stefanie Sherrill<sup>2</sup>, Nicholas Mostovych<sup>1</sup>, Sang Bok Lee<sup>2</sup> and Gary W Rubloff<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Maryland, College Park, Maryland; <sup>2</sup>Chemistry and Biochemistry, University of Maryland, College Park, Maryland.

Porous anodic alumina (PAA) templates have become an intriguing focus for nanostructured devices. The pores of conventional PAA grow in regular, uniform arrays in high density, perpendicular to the Al surface exposed to electrochemical reaction. While this vertical geometry is useful for many applications, several researchers are pursuing nanopore growth parallel to the substrate in a passivated Al layer. Forming such lateral porous anodic alumina (LPAA) encounters fundamental challenges. Most research on LPAA growth has reported only images of nanopore openings in the exposed sidewall of the oxidized aluminum layer, revealing ordering, pore diameter and interpore spacing, but not how the pores grow over their length laterally along the original Al layer. We have investigated the formation of LPAA with emphasis on understanding extended lateral growth. We first deposited a multilayer stack of thin films on a Si substrate, consisting of a bottom interface layer, an anodically active aluminum layer (100-500nm), and a top passivation layer to block vertical anodization. Using standard lithography methods, photoresist lines were patterned on top of the stack, and dry etching was used to etch through the multilayer stack to expose the Al sidewall perpendicular to the substrate. The choice of material and thickness of the top passivation layer is very critical to successful LPAA growth, since it must completely prevent anodization from above: it must be electrochemically inert under the conditions of the anodization, and thick enough to prevent penetration of the electrochemical solution to the underlying Al layer. Formation of LPAA was achieved by anodizing the aluminum layer at 40V in 0.3M oxalic acid solution. Cross-sectioned samples for SEM characterization were obtained by cleaving the samples perpendicular to the lines etched into the multilayer stack. Using SEM images, the growth rate and morphology of LPAA nanopores was estimated for various multi-layer stacks of different thicknesses and material composition as a function of top-cap thickness (100-5000nm) and top-cap material. Significant evidence emerges for the profound role of volume expansion during LPAA formation from the initial Al, which is accompanied by a volume expansion ~1.4 along the nanopore axis. Since LPAA would seem to require a geometry which confines the Al layer between two rigid layers (top passivation layer and bottom interface layer), this expansion must be absorbed by the structure. Understanding the stresses involved due to the expansion of LPAA and developing means to manage these stresses without collapse, delamination, or other adverse response of the multilayer system is critical to the growth of longer lateral nanopores. If this obstacle can be overcome to allow controlled lateral nanopore growth over longer length scales (>5μm), we foresee numerous advantages of LPAA-based devices for application and scaling of novel devices for energy storage and harvesting.

#### **P5.11**

**High Efficiency Solar Cells Based on Silole-contained Low-bandgap Polymer.** Hsiang-Yu Chen<sup>1</sup>, Jianhui Hou<sup>1</sup>, Hoichang Yang<sup>2</sup>, Guanwen Yang<sup>1</sup>, Teresa L Chen<sup>1</sup>, Wei-Lek Kwan<sup>1</sup> and Yang Yang<sup>1</sup>; <sup>1</sup>Materials Science and Eng., UCLA, Los Angeles, California; <sup>2</sup>Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

While the sun has over 60% of its photon flux in the range of 600~1000nm, using low bandgap polymers for solar cells to absorb more infrared light has become a major strategy to improve the cell efficiency. It has been estimated that polymers having a band gap smaller than 1.74 eV and a carrier mobility higher than 10-3 cm<sup>2</sup>/Vs may provide a route for power conversion efficiencies exceeding 10%. Within the categories of polymers, silole-contained polymers have been known to show high carrier mobilities. In our work, we show that by combining the advantages of small bandgap polymers and silole-contained units, a 5.6% efficiency polymer solar cell can be realized. This new polymer has a bandgap of ~1.5 eV (827nm) and a FET mobility of ~3×10<sup>-3</sup> cm<sup>2</sup>/Vs. More importantly, the film still has ~50% transparency at which the device yields 5.6% efficiency, suggesting its potential as a material for tandem or stackable solar cells. According to the experiment results, this polymer shows high crystallinity in both solution state and solid state (spin-coated film). By comparing with its carbon counterpart, we found that the replacement of the carbon atom to a Si atom transforms the structure of polymer from amorphous to highly crystalline.

#### **P5.12**

**Coarse-grained Computer Simulations of Polymer/fullerene Bulk Heterojunctions for Photovoltaic Applications.** David Mark Huang, Khanh Do, Roland Faller and Adam J Moule; Chemical Engineering and Materials Science Department, University of California, Davis, Davis, California.

Organic solar cells show promise as cheap alternatives to current silicon-based photovoltaics, but efficiencies must improve if organic photovoltaics is to become commercially viable. The active layer in organic solar cells is typically a bulk heterojunction (BHJ), in which a light-absorbing electron-donating material and an electron-accepting material are mixed together to produce a bicontinuous percolating network, thereby allowing optimization of both light absorption, which favors thicker devices (>100 nm), and charge-carrier generation and transport, which requires that photogenerated excitons be no further than the exciton diffusion length (~10 nm) from a donor-acceptor interface. The efficiency of organic solar cells depends substantially on the BHJ morphology, but prediction of the active-layer microstructure based on the constituent electron-donor and electron-acceptor phases and the processing conditions remains challenging; nano-scale morphological information is also often difficult to obtain experimentally. Molecular dynamics computer simulations can help to elucidate BHJ morphologies and to provide simple design rules for efficient organic solar cells. But the computational expense of atomistic simulations makes studying domains the size of the exciton diffusion length prohibitive. We have overcome this hurdle by developing coarse-grained models – in which collections of atoms from accurate atomistic models are mapped onto "super-atoms" – of the polymer/fullerene mixtures that are the basis of many organic BHJ solar cells. With our coarse-grained models, we have investigated the effect of the polymer:fullerene mole fraction, polymer chain length and regioregularity on the BHJ morphology, focusing on the widely used conducting polymer P3HT and fullerene derivative PCBM respectively as the electron-donor and electron-acceptor materials.

**P5.13**

**Optical Modelling of Organic Tandem Solar Cells Under Non-Normal Incident Angles** B. Viktor Andersson<sup>1</sup>, Uli Wuerfel<sup>2</sup>, Kristofer Tvingstedt<sup>1</sup> and Olle Inganäs<sup>1</sup>; <sup>1</sup>IFM, Linköping, Sweden; <sup>2</sup>Group Dye and Organic Solar Cells, Freiburg Materials Research Centre, Freiburg, Germany.

The exploitation of tandem solar cells provides the possibility to cover more of the solar spectrum when harvesting the light and thus also the possibility to enhance the power conversion efficiency (PCE). The use of organic materials is a potentially cheap way of achieving this, with the use of printing techniques for material deposition. The V-shaped solar cell is shown to be well suited for tandem configuration. In the preparation of the V tandem solar cell several single cells are prepared and organised to form a V, with the subcells placed on the inside of the legs of the V. An entering light ray experiences multiple reflections and bounces between the two sides. Together with this tandem effect the V-cell provides light trapping, caused by the multiple reflections. Thus, light harvesting is improved both as a spectral broadening and increased optical path length. Investigations of this structure have shown an enhancement of PCE of 1.8 compared to a planar cell, and simulations have shown the effect of both light trapping and tandem structure. However, these investigations have primarily been done with normal incident light. This can only be expected once a day in a real module without tracking system. A relevant quantity when dealing with real modules is the total energy delivered. The factor governing this quantity is the power output, which depends on incident angle and as a consequence the time of day. Results from optical simulations of the V solar cell with oblique incident light have been obtained. Material properties of polymer fullerene blends have been used for the active layer. A high bandgap (APFO-3:PCBM) and a low bandgap (APFO-Green5:PCBM) material blend have been used in the simulations. These materials complement each other by absorbing light at different wavelengths. Both single and tandem configurations have been used in simulations, and the results have been compared with those from simulations of planar solar cells and stacked tandem solar cells. Incident light spectra as function of the position of the sun relative the cell are used as input data, and the upper limit of the photocurrent is calculated from the photon absorption, assuming no losses of charge carriers. This means that all absorbed photons are considered to be converted to charge carriers that are collected in the outer circuit, providing an upper limit for the photocurrent. The results show that the V-shaped solar cells perform well also under oblique incident light. The light trapping mechanism is working for higher incident angles as the folding angle is decreased. The results are promising for the development of cheap solar cells with good behaviour under field conditions.

**P5.14**

**Doping of the Metal Oxide Nanostructure and Its Influence in Organic Electronics** Mi Hyae Park<sup>1</sup>, Juo-Hao Li<sup>1</sup>, Ankit Kumar<sup>1</sup>, Gang Li<sup>2</sup> and Yang Yang<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California; <sup>2</sup>Solarmer Energy Inc., El Monte, California.

We introduce a novel approach of achieving high performance organic electronic devices, based on the understanding and tuning of the properties of nano-interfacial layers. For organic electronics, the interface between organic semiconductor and metal plays a critical role in influencing device performance. It has been demonstrated that the interface can often be modified by insertion of a functional interfacial layer to improve the device performance.[1] Recently, metal oxides, such as TiO<sub>2</sub>, have been introduced in organic electronics, however, the properties are less controllable. In this presentation, a metal oxide functional interfacial layer prepared by mixing solution processable semiconducting metal oxides and salts will be introduced. The role of salts, as a source of Cs component, is found to modify the electronic property of the metal oxide. By inserting this functional layer into the polymer electronic device, we are able to tune the device property. The properties of the interfacial layer were investigated using transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS). Polymer solar cells based on poly (3-hexylthiophene) (P3HT): [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM) using Al as a cathode with the nanoscale TiO<sub>2</sub>:Cs interfacial layer exhibited excellent characteristics with a power conversion efficiency of 4.2%. The effectiveness of this unique functionality also extends to polymer light emitting devices, where a lower driving voltage, improved efficiency, and extended lifetime are demonstrated. [1] Huang, J.; Xu, Z.; Yang, Y. *Adv. Funct. Mater.* 17, 1966-1973 (2007)

**P5.15**

**Spinning Electroactive NanoFibers and NanoArchitectures for Energy Storage Conformal Coatings** Cheng Huang, Energy & Environment Directorate, Battelle, Pacific Northwest National Laboratory, Richland, Washington.

Engineering electroactive materials sciences are towards transformational science and technology for revolutionary applications in energy, electronics, defense, and life systems. The solution processes provide a very simple, cost-effective way to fabricate the electroactive architectures, especially for electrical storage and conversion. Multifunctional multiscale electroactive material thin-film coatings are made by combinational solution processes such as screen printing, digital inkjet printing, spinning and spraying techniques. Spinning and spraying could produce uniform, conformal coating in a very controlled manner, providing more options for different structures and applications because of their superior conformal coating capability down to nano scale. In this talk, we first review the proposed 2D delocalized charge molecular systems and the development of related conductive polymeric and carbon macromolecular materials, as high-performance electroactive nanoniks, including phthalocyanine oligomeric nanosheets, aniline oligomeric nanosheets, and graphene nanosheets. Then we focus on spinning nanofibers and nanoarchitectures from electroactive polymeric and electroceramic oxide to control and optimize the storage and transport of charged species.

**P5.16**

**Understanding the Device Physics of Self-Assembling "Shuttlecock" Fullerenes In Bulk Heterojunction Photovoltaics.** Alexander Ayzner, Chemistry, UCLA, Los Angeles, California.

Self-organizing "shuttlecock" fullerene derivatives have been synthesized and utilized as electron acceptors in P3HT-based bulk heterojunction photovoltaics (PVs). By varying the substitution pattern on the periphery of the fullerene, robust 1-D stacking motifs are observed in the fullerene crystal structure. Here we concentrate on two model shuttlecocks - one that self-assembles into 1-D wires in the solid state and one that does not; we find that upon thermal annealing, devices made with derivatives that form the 1-D wires yield PVs with significantly higher efficiencies relative to fullerenes that do not form 1-D columnar assemblies in the crystal state. X-ray diffraction studies suggest that the different fullerene substitution patterns have a very large effect on the degree of polymer crystallization. We also find that the device performance is relatively insensitive to fullerene loading, consistent with the view that these self-assembling molecules form nano-wire-like domains in the device, which are responsible for the photovoltaic effect with blended with P3HT.

**P5.17**

**Design of 3-dimensional Textured Organic Solar Cells.** Kanwar Nalwa<sup>1</sup>, Baskar GanapathySubramian<sup>2</sup> and Sumit Chaudhary<sup>1</sup>; <sup>1</sup>Electrical and Computer Engineering, Iowa State University, Ames, Iowa; <sup>2</sup>Mechanical Engineering, Iowa State University, Ames, Iowa.

Organic materials are attractive for photovoltaics primarily because of the prospect of high throughput manufacture using reel-to-reel or spray deposition. In the formation of polymer based photovoltaic devices, the aspect that limits the power conversion efficiency is the short diffusion length of the excited states (excitons) in polymers, in the range of 10-20nm. Optical absorption length, which is in the range of 50-100nm and much larger than the exciton diffusion length, poses the limit on charge generation. It is important to achieve complete optical absorption for active layers much thinner than optical absorption length to minimize losses due to recombination of charge carriers. Previously, light trapping techniques have been coupled with organic solar cell but without any significant success. Three dimensional sub micron grating structure is analyzed using finite element method (FEM) simulations for finding the optical absorption in different layers of solar cell to optimize the photonic concentrator effect of the grating structure. The electromagnetic wave equation is solved on the entire defined geometry taking into account the interference effects as well as the effects of refraction and reflection. The energy dissipation of electromagnetic field in the active layer is studied as a function of active layer thickness, grating pitch and height. The superiority of grating structure in terms of light trapping feature as compared to planar geometry is clearly demonstrated by simulation results.

**P5.18**

**Multi-walled Carbon Nanotubes Electrodes for the All Vanadium Redox Flow Battery.** Chang-Chung Yang<sup>1</sup>, Ssu-Tai Lin<sup>1</sup> and Bo-Ying Chen<sup>1,2</sup>; <sup>1</sup>Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan; <sup>2</sup>Department of Materials Engineering, Ming Chi University of Technology, Taipei, Taiwan.

Renewable energy sources, like solar or wind energy, have emerged as the potential distributed power generation system. Since the power leveling is a critical issue in renewable energy, energy storage technologies provide an alternative solution to the problem of balancing power generation and power consumption. In this research, one kind of storage system called all vanadium redox flow battery has been focused on to improve its performance. The all vanadium redox flow battery is one of the most preferred flow batteries for a number of reasons, including the lack of cross contamination, due to the same metal ion in both electrolytes. The slow reaction kinetics on the electrodes of carbon felts is the major drawback of all Vanadium redox flow battery which limited its efficiency of charge and discharge. In this research, multi-walled carbon nanotubes (MWNT) were prepared on the surface of carbon felt by water-assisted ethylene pyrolyzing chemical vapor deposition. Each MWNT grew from the surface of fibers in the texture of carbon felts and obviously improved the effective specific area of original electrodes of carbon felts. For the catalyst of MWNTs growth, a double layer of Ti layer with 3 nm in thickness and followed by Fe with 7nm was deposited onto the carbon felts by thermal evaporation in the vacuum chamber with 10<sup>-6</sup> torr. The diameter of each carbon fiber in the felts is around 7.3μm±0.5μm. In the MWNT growth, the mixed gas Ar/H<sub>2</sub> (600 sccm/400 sccm) was introduced to quartz tube furnace and the Ti/Fe catalysts was annealed at 700~1000 degree C for 10min. Then, ethylene (50~200 sccm) and little content of water

vapor by passing a small fraction of Ar carrier gas (30~150 sccm) through a water bubbler were introduced into the gas mixture to start CNTs synthesis. The growth time was varied from 2.5 to 40 min. The diameter of MWNTs on the fibers is around 70nm±10nm and the appearance of each carbon fiber is like a fury brush. The effects of processing gas flow rate, growth time, and water vapor content on the growth of MWNTs on the felt electrodes were systematically studied. A prototype of a redox flow battery cell has been developed to enable the flexible testing on electrodes, membranes and electrolytes. The typical charge and discharge behavior was demonstrated. The battery was charged by a constant current to a voltage of 2.5V and completely discharged. The efficiency of MWNT electrodes has 14% improvement compared to original electrodes. In the following research, some active catalysts, like nickel or palladium, would be deposited on the MWNTs to further improve the reaction kinetics on electrode to enhance to battery efficiency.

#### P5.19

**Three Dimensional Architectures for the Miniaturization of Batteries and Their Constraints.** Nicolas Cirigliano<sup>1</sup>, Peter Malati<sup>1</sup>, Janet Hur<sup>2</sup>, Sarah Tolbert<sup>3</sup>, Chang-Jin Kim<sup>2</sup> and Bruce Dunn<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California; <sup>2</sup>Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California; <sup>3</sup>Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California.

Commercial two dimensional batteries based on these designs share the common property of planar stacking of active materials. Conventional batteries offer a high energy density due to the large volume of material used to store charge, but are limited to low current densities because of long diffusion paths. Thin-film batteries minimize the diffusion problem and can achieve higher power densities. However energy densities are so small that they require a large footprint area for practical uses. Because of the limitations with 2D designs, we have begun to investigate three dimensional geometries, which can potentially provide both high energy density and high power density. The present paper is directed at the design of 3D battery architectures and the calculation of their energy densities. Three dimensional batteries share the common feature of being able to increase energy densities by creating electrode architectures which can be built up in a skyscraper fashion, rather than built out, resulting in a 3D matrix of active materials. Currently, multiple 3D battery designs exist. The most notable of these are an interdigitated design, consisting of alternating anode and cathode posts immersed in electrolyte, and a continuous concentric tube design in which an array of cylindrical electrode posts are coated conformally with electrolyte while any remaining volume is filled by the opposite electrode material. In every 3D design, it is vital to maintain high energy densities while simultaneously keeping transport distances small to ensure high power densities. Our results with 3D Zn-air batteries demonstrated that high aspect ratio (length:diameter) rods are essential to exhibiting high energy densities. The next step is to apply the same design methods to secondary lithium-ion batteries, with the ultimate goal being the fabrication of electrodes based on incorporating extremely high aspect ratio nanorods or nanotubes. The resulting calculations identify the level of capacity expected from the electrodes. Using these results, we will be able to determine the operating parameters for the 3D batteries as well as to establish the maximum height at which electrode rod resistance becomes too large for Li intercalation.

#### P5.20

**Low Potential Reactivity of Transition Metal Oxide Aerogels and Mesoporous Films with Lithium** Veronica Augustyn<sup>1</sup>, Bruce Dunn<sup>1</sup> and Sarah Tolbert<sup>2</sup>; <sup>1</sup>Materials Science & Engineering, University of California, Los Angeles, Los Angeles, California; <sup>2</sup>Chemistry & Biochemistry, University of California, Los Angeles, Los Angeles, California.

Currently, lithium ion batteries store charge in layered electrode materials, such as graphite and LiCoO<sub>2</sub>. However, intercalation is not the only way that materials may interact with lithium ions. In some metal oxides, lithium can also react to form Li<sub>2</sub>O and metal nanoparticles through conversion reactions. Depending on the valence of the metal element, these reactions may result in very high capacity. Research has shown that conversion reactions are reversible using nanoparticles, meaning the material can sustain repeated charge/discharge cycles. This is a dramatic difference from bulk behavior, where metal oxides with close packed structures would break apart from the conversion reaction. To further examine this phenomenon, we have been researching aerogels and mesoporous films, which contain nanodimensional features. The unique morphology of these high surface area materials leads to a three dimensional architecture that allows for increased electrolyte penetration, and should give rise to more electrochemically active surfaces and faster electron transfer processes than those found in traditional two dimensional electrodes. The high valence of vanadium (+5) offers the possibility of charge storage at low potentials. Theoretical calculations show that for V<sub>2</sub>O<sub>5</sub>, lithium may react to form suboxides such as V<sub>2</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>3</sub>, etc. and Li<sub>2</sub>O at potentials at or below 1V (vs.

Li/Li<sup>+</sup>). V<sub>2</sub>O<sub>5</sub> aerogels synthesized with the supercritical drying technique exhibit a morphology consisting of interconnected nanoparticle ribbons. Galvanostatic discharge experiments with these materials show considerable reversible capacity below 1.5V, in excess of 500 mAh/g, which may be associated with conversion reactions. These results have led to the investigation of mesoporous metal oxide films, which can be processed into highly ordered nanocrystalline structures that further increase electrolyte penetration and require no additional conductive additives. High surface area V<sub>2</sub>O<sub>5</sub> aerogels and mesoporous films are materials that show promise for low potential lithium reactivity, and may lead to high capacity electrodes for lithium ion batteries.

#### P5.21

**Hetero-Nanostructures for Acceleration of Electrochemical Reaction in SOFC Electrodes** Kazuyoshi Sato, Satoshi Ohara, Makio Naito and Hiroya Abe; Osaka University, Ibaraki, Japan.

In this study, we introduce a strategy on fabrication of electrochemically active electrodes in solid oxide fuel cell, based on the synthesis of nano-sized composite particles and the reduction of sintering temperature. Nano-sized composite particles were

synthesized by a wet chemical route developed in our laboratory. The average crystalline size of them was less than 10 nm even their precursor was crystallized at 600- 800 deg C. The composite particles were deposited on YSZ substrate by a novel direct coating technique. Although the fabricated electrode layer can be sintered at significantly lower temperature compared with the conventional particles, the nanostructure was stable at operation condition due to well organized three dimensional networks. The electrodes provided considerably low polarization resistance even at 800 deg C or less.

#### P5.22

**Quantitative Quartz Crystal Microbalance Studies of Equilibrium Pressures in Thin Film Metal Hydrides.** Erkan Senses, Stephen T Kelly and B. M Clemens; Materials Science and Engineering, Stanford University, Stanford, California.

Many three dimensional architectures designed for energy generation and storage are created by using nanostructures involving large amount of interfacial density. In order to design effective 3D structures for energy storage, the effects of this small size and interfacial density on thermodynamics and kinetics should be well known. The objective of this work is the study of thermodynamic properties of metal hydride thin films and how these properties change with reductions in critical dimension. For this purpose, equilibrium pressures of Mg-MgH<sub>2</sub> system are obtained by monitoring the resonance frequency of a Quartz Crystal Microbalance (QCM) which is extremely sensitive to mass change. According to continuum modeling, as the size of the particles becomes smaller, the interface energy tends to change the equilibrium pressure. In order to observe this, we deposited thin films containing alternative layers of Mg and Pd. By changing the thicknesses of the layers, we are able to change the size from bulk to critical dimensions in order to obtain different amount of interface area per volume in the films. The equilibrium pressures obtained from QCM measurements are compared to the results obtained from continuum modeling. In addition, we doped Mg films with Ti in order to investigate its effect on equilibrium pressure.

#### P5.23

**Photovoltaic Devices Based on Heterojunctions of TiO<sub>2</sub> Nanotube Arrays and P3HT.** Tae-Sik Kang<sup>1,2</sup>, James R Deneault<sup>1,2</sup>, Bamey E Taylor<sup>1,2</sup> and Michael F Durstock<sup>1</sup>; <sup>1</sup>Air Force Research Laboratory, Wright Patterson AFB, Ohio; <sup>2</sup>Universal Technology Corporation, Dayton, Ohio.

Polymer-based photovoltaic materials and devices are attracting more and more attention due to the possibility of creating low-cost, light-weight, and large area solar cells. Vertically oriented TiO<sub>2</sub> nanotube arrays formed by alumina templating and sol-gel infiltration has been developed. Heterojunction films containing TiO<sub>2</sub> nanotube arrays infiltrated with poly(3-hexylthiophene) (P3HT) were prepared. In this architecture, TiO<sub>2</sub> and P3HT act as the electron acceptor and donor, respectively. The film morphology was studied by electron microscopy, X-Ray diffraction, and diffuse reflectance FTIR spectroscopy. The TiO<sub>2</sub> nanotubes have the desired stoichiometric chemical composition and the anatase crystal structure after firing at 500oC for 30 minutes. In addition, P3HT adheres readily to all TiO<sub>2</sub> nanotube surfaces. Complete photovoltaic devices were successfully fabricated and studied under standard solar simulation conditions as well as variable light intensity. The effects that the film morphology has on these device performance characteristics will be discussed.

#### P5.24

**Electrochemical Synthesis of Sn-Conducting Polymer Composite Electrodes for Use in Secondary Li-Ion Batteries.** Nikhilendra Singh, Yongju Jung and Kyoung-Shin Choi; Chemistry, Purdue University, West Lafayette, Indiana.

Tin (Sn) has been identified as a suitable material for the anode in lithium-ion secondary batteries due to its superior theoretical capacity (992 mAh/g) compared to conventionally used graphite anodes (372 mAh/g). However, the charging and discharging reactions of Sn are based on the formation of a Li<sub>x</sub>-Sn alloy ( $\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \rightarrow \text{Li}_{4.4}\text{Sn}$ ) that involves a severe volume change (ca. 300%). This stress eventually degrades the electrode and results in the formation of pulverized Sn, leading to poor cyclic performance. In this presentation, we report a new Sn-Polypyrrole (PPy) composite electrode where Sn nanoparticles are well dispersed among the PPy framework. This structure allows for stress free expansion and contraction of the active material (Sn) during Li<sub>x</sub>-Sn alloying and de-alloying processes, alleviating the pulverization problem. The Sn-PPy composite electrodes were prepared via a new electrochemical synthesis mechanism recently developed in our laboratory. It allowed for the fabrication of Sn-PPy composite electrodes directly from a conducting substrate and eliminated the use of binding materials and conducting carbon used in current batteries, simplifying the fabrication procedure. The inactivity of PPy in the potential range applied for the charging and discharging reactions also ensures Sn as the only active material in the composite. The detailed synthesis mechanism and characterization of the Sn-PPy composite electrodes will be presented. The performance of Sn-PPy composite electrodes and pure Sn electrodes as anodes for the secondary Li-ion batteries will also be compared and discussed.

#### P5.25

**Preparation and Electrochemical Capacitive Properties of Electrospun RuO<sub>2</sub> Nanofiber Mats.** Tae-Seon Hyun<sup>1,2</sup>, Jae-Min Hong<sup>2</sup>, Ho Gi Kim<sup>1</sup> and Il-Doo Kim<sup>2</sup>; <sup>1</sup>Materials Science and engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea, South; <sup>2</sup>Nano Electric Materials, Korea Institute of Science and Technology, Seoul, Korea, South.

Recently, electrochemical energy storages developed using nanotechnology have attracted intensive attention due to their high capacity, long term stability and fast response time. In particular, ruthenium oxide (RuO<sub>2</sub>) is of interest active materials for application in electrochemical capacitor due to its low resistivity of ~ 35  $\mu\Omega\text{cm}$ , high redox reactivity and high chemical stability. In

this work, we prepared conducting RuO<sub>2</sub> nanofiber-mats, consisted of the particle with the size of tens nanometer, by the electrospinning method. The RuO<sub>2</sub> nanofibers, which were calcined at 400°C for 30min after hot-pressing process, showed an interconnected shape such as cross-linked network. These nanofiber-mats exhibited a high porosity of 58 m<sup>2</sup>/g based on BET measurement. The resistivity of crystalline RuO<sub>2</sub> nanofiber-mats was as low as 3.4X10<sup>-3</sup> Ωcm . Using the subsequent coating treatment of hydrous RuO<sub>2</sub> by electrodeposition on the surface of RuO<sub>2</sub> nanofiber mats, stacked electrodes of hydrous RuO<sub>2</sub>/ RuO<sub>2</sub> nanofiber mats were successfully prepared on Ti current collector for application in electrochemical capacitor. The specific capacitances were measured by cyclic voltammetry over a voltage range of 0-1.0 V at various scan rates in electrolyte solution of 1.0 M H<sub>2</sub>SO<sub>4</sub>. Crystalline RuO<sub>2</sub> nanofiber-mats calcined at 400°C showed a low specific capacitance of 31.3 F/g. On the other hand, the specific capacitance value of RuO<sub>2</sub> nanofiber-mats coated by hydrous RuO<sub>2</sub> increased up to 843 F/g at a scan rate 10mV/sec. It is important to note that the capacity loss was 25 % up to the scan rate of 2000 mV/sec Fast characteristic response time of 0.05 sec was observed in stacked electrodes of hydrous RuO<sub>2</sub>/ RuO<sub>2</sub> nanofiber mats.

#### **P5.26**

**Characteristics of Polymer Solar Cell with Ag Nanoparticles using Solution Process.** Tae-Soo Kim<sup>1</sup>, Seok-In Na<sup>1</sup>, Jo Jang<sup>1</sup>, Seok-Soon Kim<sup>2</sup> and Dong-Yu Kim<sup>1</sup>; <sup>1</sup>Material Science and Engineering, Gwangju Institute of Science and Technology(GIST), Gwangju, Korea, South; <sup>2</sup>School of Materials Science & Chemical Engineering, Kunsan National University, Kunsan, Korea, South.

Polymer solar cells (PSCs) are the promising candidates for renewable energy sources. To commercialize PSCs, higher efficiency and cheaper process are needed. In the present, many research groups have investigated the applications of metal nanoparticles (NPs) such as silver (Ag) and gold to organic solar cells. It has been reported that some organic solar cells containing metal NPs show the improvement of the efficiency due to metal NPs' surface plasmon resonance (SPR). In this work, PCS was based on P3HT:PCBM bulk heterojunction system. Ag NPs were embedded in PCS's layers using solution process, which is an important factor in low-cost roll-to-roll process. Effects of these Ag NPs on the performance of PSCs were investigated. More detailed studies were also performed through UV-vis absorption, scanning electron microscope (SEM), incident photon to current conversion efficiency (IPCE), and current density-voltage (J-V) measurement.

#### **P5.27**

**Synthesis of High-Density CdS Nanowires on Conductive Glass Substrates for Hybrid Solar Cell Applications** Jung-Chul Lee and Yun-Mo Sung; Materials Sci. & Eng., Korea University, Seoul, Korea, South.

Owing to distinct electrical and optical properties, organic/inorganic hybrids has shown strong potential to be used for high-performance devices including sensors, displays, light emitting diodes, solar cells, refractive and anti-refractive materials, and so on. In particular, organic/inorganic hybrid solar cells show technological importance due to advantages, such as low cost, easy fabrication, and the possibility to fabricate flexible devices, compared to inorganic solar cells. In accordance with the need in hybrid solar cells, various inorganic semiconductors, such as CdSe, CdTe, CdS, and PbS, have been actively investigated because of their application to serve as an acceptor for hybrid solar cells. CdS is a II-VI semiconductor having a direct band gap of 2.4 eV at room temperature and it has been known as one of the most promising photo-sensitive materials owing to its unique photochemical activities and strong visible-light absorption and emission. In this study, we for the first time demonstrate the success in the vapor-phase synthesis of CdS nanowires at a remarkably reduced temperature of ~450 oC that is compatible with transparent conducting oxide-coated soda-lime glass substrates. Bi catalyst layer and polyvinyl alcohol (PVA) played a major role in the low temperature synthesis of high-quality CdS nanowire arrays. CdS nanowires were defect free single crystalline wurtzite crystals and they were 50~100 nm and 2~5 μm in diameter and length, respectively. The mechanism was discussed in detail for nanowire growth at a reduced temperature. CdS nanowires were combined with poly [2-methoxy-5-(2'-ethylhexyloxy)-1, 4-phenylenevinylene] (MEH-PPV), a conjugated polymer to form organic/inorganic hybrids. The light absorption and light emission properties of MEH-PPV/CdS hybrids were investigated. Also, the photovoltaic properties were investigated for polymer/CdS hybrid solar cells.

#### **P5.28**

**Molecular Dynamics Modelling a 3D-MB Electrode/Electrolyte Interface** Daniel Brandell, Materials Chemistry, Uppsala University, Uppsala, Sweden.

The development of three-dimensional architectures for Li-ion microbatteries places new demands on both electrode and electrolyte materials. Typically, high ionic conductivity of the electrolyte becomes a less stringent requirement, while good mechanical stability becomes more important. At the same time, it also becomes more important to utilize the full theoretical capacity of the electrode materials. In this context, it is therefore vital to acquire a more complete picture of the electrochemical processes occurring at the electrode/electrolyte interface, e.g., the Li-ion intercalation and de-intercalation processes. Furthermore, with electrolyte dimensions on the micrometer scale, the Solid Electrolyte Interphase (SEI) becomes a significantly larger proportion of the electrolyte. This makes ionic conductivity mechanisms through the SEI more decisive for the performance of the entire battery. Computer simulation and modelling can give insights into the structure and dynamics of the 3D-MB system at dimensions generally inaccessible to experimental techniques. In particular, Molecular Dynamics (MD) simulation can probe atomic structure and transport mechanisms on time- and length-scales relevant to both homogeneous and heterogeneous regions of the system. MD can also be used to identify or predict the formation of sub-structures or regions in the battery where the values

of certain properties, such as local ion diffusion coefficients, can diverge from those elsewhere in the system. The electrode/electrolyte interface between LiFePO<sub>4</sub> and LiPF<sub>6</sub>(PEO)<sub>x</sub> for x = 6 and 10 has here been investigated by MD simulation techniques for both crystalline and amorphous short-chain polymer electrolyte conformations. The size and shape of different regions are identified in the SEI formed. The atomic interaction across the interface - the polymer bonding to the phosphate - is characterized, and the Li-ion transport mechanisms are studied by imposing a realistic external electric field on the MD box. Local diffusion coefficients needed for larger-scale simulations (such as Finite Element Analysis) are derived.

#### P5.29

**Fabrication of Ordered Arrays of Mesoporous Carbon Spheres.** Zhongjiong Hua<sup>1</sup>, Lianbin Xu<sup>1,2</sup>, Fei Wang<sup>1</sup>, Yushan Yan<sup>2</sup>, Anvar A Zakhidov<sup>3</sup>, Ray H Baughman<sup>3</sup> and Jian-Feng Chen<sup>1</sup>; <sup>1</sup>Key Lab for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing, China; <sup>2</sup>Department of Chemical and Environmental Engineering, University of California at Riverside, Riverside, California; <sup>3</sup>NanoTech Institute, University of Texas at Dallas, Richardson, Texas.

Three-dimensionally (3D) ordered arrays of mesoporous carbon spheres were fabricated through a combination of self-assembly and multiple templating methods including hard-templating and soft-templating techniques. A 3D ordered poly(methyl methacrylate) (PMMA) inverse opal was prepared by templating a silica colloidal crystal (opal). After removal of the silica spheres, carbon precursor, consisting of amphiphilic triblock copolymer Pluronic F127 as a structure directing agent and phloroglucinol as a carbon source, was infiltrated into the void space of the PMMA inverse opal. Subsequent thermal curing and carbonization produced 3D ordered arrays of mesoporous carbon spheres. Details on the fabrication and characterization of these materials are presented including scanning electron microscopy, transmission electron microscopy, and nitrogen adsorption studies.

#### P5.30

**Power Generation With Laterally Packaged Piezoelectric Fine Wires.** Rusan Yang<sup>1</sup>, Yong Qin<sup>1</sup>, Liming Dai<sup>2</sup> and Zhong Lin Wang<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Department of Chemical and Materials Engineering, University of Dayton, Dayton, Ohio.

Converting mechanical energy into electricity has unique applications in sensing, medical science, defense technology and personal electronics<sup>1</sup>. Nanowires (NWs) have been demonstrated as unique materials for energy scavenging, with potential for powering nanodevices. Previously reported piezoelectric NW nanogenerators are based on vertically aligned ZnO NWs that are rooted at a substrate and are free at tips. The contact between the electrode and the NWs is transiently on and off for each cycle of the driving action. Problems with their output stability, mechanical robustness, life time, environmental adaptability and washability are yet to be addressed. We report here a flexible power generator that is based on cyclic stretching-releasing of a piezoelectric fine-wire (PFW) [1, 2], which is firmly contacted at two ends with metal electrodes, laterally bonded and packaged on a flexible substrate. When the PFW is stretched as driven by substrate bending, a piezoelectric-potential-drop is created along the PFW, which acts as a "capacitor" and "charge pump" that drives the back and forth flow of electrons in the external circuit to achieve a charging and discharging process when the PFW is stretched and released, respectively. A repeated stretching-releasing of a single PFW with strain of 0.05-0.1% creates an oscillating output voltage up to ~50 mV. The energy conversion efficiency of the wire itself is up to 6.8%. The reported work demonstrates a new approach towards robust, no sliding-contact technology for mechanical energy harvesting. [1] R.S. Yang, Yong Qin, Liming Dai, and Z.L. Wang, Nature Nanotechnology in press. [2] <http://www.nanoscience.gatech.edu/zlwang/>

#### SESSION P6: Nanostructured Materials for Capacitors

Chairs: Debra Rolison and Patrice Simon  
Thursday Morning, April 16, 2009  
Room 2022 (Moscone West)

##### 8:30 AM \*P6.1

**Nanoporous Carbon-based Micro-supercapacitor.** Patrice Simon<sup>1</sup>, David Pech<sup>3</sup>, Hugo Durou<sup>3</sup>, Magali Brunet<sup>3</sup>, Pierre-Louis Taberna<sup>1</sup> and Yury Gogotsi<sup>2</sup>; <sup>1</sup>CIRIMAT, Université Paul Sabatier, Toulouse, France; <sup>2</sup>Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; <sup>3</sup>LAAS, Université Paul Sabatier, Gainesville, Florida.

Electrochemical Capacitors (EC), also called supercapacitors, store energy using either ion adsorption (electrochemical double layer capacitors, EDLC) or fast surface redox reactions (pseudo-capacitors). They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. In the same way as batteries, micro-supercapacitors are today focusing increasing interest for power buffer or energy harvesting applications and this presentation will be focused on the nanostructured materials synthesis and their characterization for micro-supercapacitor applications. In a first part, we will expose results obtained with nano-porous carbons, namely the Carbided-Derived Carbons (CDCS), that allowed us to improve our basic understanding in charge storage mechanisms in nanostructured carbons with pore size less than 1 nm. The use of a three-electrode cell configuration made possible the discrimination between anion and cation adsorption. Capacitance vs pore size plots have been obtained for both ions in two different electrolytes: ACN + 1M NEt<sub>4</sub>BF<sub>4</sub> and a solvent-free electrolyte (EMI,TFIS ionic liquid). The results confirmed that ions must be desolvated for entering micropores, and that the optimum pore size needed to maximize the capacitance is close to the ion size. Fine-tuning the carbon pore size versus the ion size could lead in the near future to the design of high-energy density Electrochemical Double Layer Capacitors. In a second time, we will show the first results obtained for the integration on silicon of a micro-supercapacitor using nanoporous carbons. The developed micro-supercapacitor consists in two interdigitated gold electrodes on oxidised 4" silicon wafer. On these electrodes, the active material film is deposited using the ink-jet technique. Careful functionalisation of the surfaces (silicon

versus gold) had been developed to achieve selective coverage of the gold electrodes by the active material film, with a resolution of 40 µm. After active material deposition (few µm thick), the prototypes were bonded and tested with propylene carbonate + NET4BF4 (1M) electrolyte through impedance spectroscopy and cycling voltammetry. A capacitance of 1 µF (700 nF/sq.mm) was measured, which is 10 times higher than an interdigitated structure without active material. Future developments will consist in depositing thicker active material, optimising the active material itself and provide full device encapsulation. This new technology could address the need for mobile integrated energy storage

#### 9:00 AM P6.2

**Atomic-Scale Impurity Identification and 3-D Morphology of Mesoporous Carbide-Derived Carbons.** Ilke Arslan<sup>1</sup>, Scarlett Widgeon<sup>1</sup>, Mhairi Gass<sup>2</sup>, Andrew Bleloch<sup>2</sup>, Sun-Hwa Yeon<sup>3</sup> and Yury Gogotsi<sup>3</sup>; <sup>1</sup>Chemical Engineering and Materials Science, University of California-Davis, Davis, California; <sup>2</sup>UK SuperSTEM Laboratory, Daresbury Laboratory, Daresbury, United Kingdom; <sup>3</sup>Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

World energy consumption is projected to double in less than 50 years and more than triple before 2100. These dramatic needs demand new, clean, renewable sources of energy to reduce CO2 emissions and other harmful greenhouse gases that contribute to global warming, and eliminate our nation's dependence on foreign oil. While the production of electricity from clean sources such as solar, wind, and nuclear have been prioritized, an equally pressing concern is how to store this electricity and have it reliably and readily available at all hours of the day. Efficient electrical energy storage (EES) has the potential for large impact in commercial and residential grid applications, and in allowing hybrid vehicles to move towards plug-in hybrid electric vehicles, or even all-electric vehicles. Nanostructured carbon materials are playing a key role in the development of electrodes for better batteries and supercapacitors. A fundamental understanding of the disordered carbon electrode materials with a non-periodic structure, and particularly the pore surfaces where charge storage occurs, is necessary to move the EES technology forward. Here we use a combination of atomic-resolution imaging, atomic-resolution electron energy-loss spectroscopy (EELS), and three dimensional imaging in the scanning transmission electron microscope (STEM) to study carbide-derived carbons (CDC), a class of porous carbons that allow for more control over pore size and have a high specific surface area. These electrode materials will intrinsically contain impurity atoms that cannot be fully removed during synthesis. Our preliminary results show that in some materials, the impurity atoms segregate to the surfaces of the pores, with pore sizes in the range of 5-6 nm or 15-16 nm, depending on the material. This segregation will obviously change the surface chemistry and ability of the surfaces to retain charge. Results will be discussed from CDC samples produced by chlorination of SiCN and Ti2AlC precursors.

#### 9:15 AM P6.3

**PPO-PEO-PPO Block Copolymer Assisted Synthesis of Three Dimensional Carbon Aerogels Exhibiting High Conductivity and Remarkable Capacitance.** Francisco del Monte<sup>1</sup>, Maria L. Ferrer<sup>1</sup>, Maria C. Gutierrez<sup>1</sup>, Fernando Pico<sup>1</sup>, Jose M. Rojo<sup>1</sup>, J.Manuel Amarilla<sup>1</sup>, F. Javier Palomares<sup>1</sup> and Fausto Rubio<sup>2</sup>; <sup>1</sup>ICMM-CSIC, Madrid, Spain; <sup>2</sup>ICV-CSIC, Madrid, Spain.

This work describes a PPO15-PEO22-PPO15 assisted synthesis for the preparation of highly porous (ca. 65%) and ultralightweight (specific gravity 5×10-2) monolithic CA. The resulting carbon aerogels exhibited a continuous 3D network structure built of sintered carbon spheres which allowed the achievement of a remarkably high electric conductivity (~2.5 Scm-1). CA monoliths also exhibited a bimodal macro- and microporous structure, the former due to the voids left among sintered carbon spheres and the later due to the microporous character of the carbon spheres induced by the use of PPO15-PEO22-PPO15 in the synthesis. Such a structure was highly suitable for EDL, with the macroporous network structure providing an efficient transport of electrolyte throughout the monolith and the microporosity being crucial for the formation of double layer at the electrode/electrolyte interface. This feature was indeed reflected in the achievement of remarkable values of capacitance, ranging from 180 to 225 F/g (normalized by mass of CA monolith) and from 25 to 31 microF/cm<sup>2</sup> (normalized by BET surface area of CA monolith) depending on the electrolyte solution (KOH or H<sub>2</sub>SO<sub>4</sub>, respectively). Such a high volumetric capacitance offers potential advantage for supercapacitor applications, especially for the design of energy storage devices of high energy and power density.

#### 9:30 AM P6.4

**Multifunctional Carbon Nanoarchitectures as Designer Platforms for Electrochemical Power Sources.** Jeffrey W. Long<sup>1</sup>, Megan E Bourg<sup>1</sup>, Justin C Lytle<sup>1</sup>, Anne E Fischer<sup>2</sup>, Katherine A Pettigrew<sup>2</sup>, Jennifer L Dysart<sup>1</sup>, Debra R Rolison<sup>1</sup> and Azzam Mansour<sup>3</sup>; <sup>1</sup>Code 6170, Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Nova Research, Inc., Alexandria, Virginia; <sup>3</sup>Naval Surface Warfare Center - Carderock Division, West Bethesda, Maryland.

Carbon aerogels and nanofoams are used as the basis for 3-D multifunctional nanoarchitectures that are designed as electrode structures for applications ranging from high-rate Li-ion batteries and electrochemical capacitors to fuel cells. The inherent structural characteristics of carbon aerogels/nanofoams—high surface areas and through-connected networks of porosity with tunable pore sizes—not only enable rate-critical performance in electrochemical applications, but also facilitate the modification of the interior carbon surfaces with functionalities that store charge (metal oxides, electroactive polymers) or exhibit electrocatalytic activity (metal nanoparticles and/or metal oxides). For example, we recently demonstrated a simple self-limiting redox deposition process that yields conformal nanoscale manganese oxide coatings that permeate the macroscopic thickness (0.1-0.2 mm) of carbon-paper-supported nanofoam structures. In the resulting multifunctional electrodes, the redox reactions of the nanoscopic metal-oxide phase provide high charge-storage capacity, while the conductivity and high-quality pore structure of the carbon nanofoam facilitates the efficient transport of electrons and ions, respectively, for optimal high-rate performance. Although such electrode structures are readily incorporated as individual cathodes or anodes in conventional battery and electrochemical

capacitor designs, they may also be used as the basis for 3-D integrated battery architectures, in which the remaining free volume of the structure is sequentially filled with a nanoscale polymer electrolyte and opposing electrode phase.

#### 9:45 AM P6.5

**Nanosheets-based Lithium Ion Capacitor.** Feng Li, Dawei Wang, Gang Liu, Zhi-gang Chen, Zhongshui Wu, Wencai Ren and Hui-ming Cheng; Institute of metal research, CAS, Shenyang, China.

In recent years, many electrochemical devices have been explored for reversible energy storage in response to the ever increasing demand for clean energy and climate change mitigation technologies. Lithium ion capacitor (LIC) integrating different energy storage modes are highly promising as potential high density energy storage devices for a wide range of applications such as portable electronics and electric vehicles, etc., many of which require high energy-density and power-density storage. Intercalation/double layer type LIC is usually constructed with carbon or titania anode and carbon cathode. Now two kind of titania and graphene nanosheets were explored widely. Graphene, as an atomic monolayer material with carbon atoms regularly arranged in two-dimensional honeycomb lattice, is becoming a new star in nanosheets fields. Titania nanosheets, another important kind of nanosheets materials, can be prepared through easy chemical exfoliation way. The unique two-dimensional structure of titania nanosheets render them different electrochemical behavior in lithium storage, compared with titania nanoparticles, nanotubes or nanowires. Here, we assembled intercalation/electric double layer type LIC using nanosheets-based materials. Graphene materials with interesting chemical and physical properties were tested as cathode materials for LIC, and titania nanosheets were examined for LIC anode materials. The present device construction can deliver the maximum energy density of 36 Whkg<sup>-1</sup> and the largest power density of 2556 Wkg<sup>-1</sup>.

#### 10:30 AM P6.6

**Modeling of 3-D Energy Storage in Carbon Nanotube Ultracapacitor.** Antonis A Orphanou, Toshishige Yamada and Cary Y Yang; Electrical Engineering, Santa Clara University, Santa Clara, California.

Until recently, efforts to enhance the energy storage capability of passive components such as capacitor have primarily concentrated on the increase of the capacitor's charge-storage surface area. Using the capacitor as an energy storage device has so far been a two-dimensional problem, aiming to maximize the electrodes' surface areas. The introduction of activated carbon, despite its limitations, is becoming an attractive alternative option for optimal energy storage capacitors. Efforts on using nanotubes as an alternative to activated carbon have been reported [1]. The porous carbon is replaced by a "forest" of nanotubes, resulting in claims that the nanotubes can increase by as much as 50% the capacitors' energy storage capability [1]. With the technology for growing nanotubes on metallic substrates now available, this is a very promising step towards a more effective energy storage component. The nanotube "forest" has added an extra dimension that needs to be analyzed and understood. A traditionally 2-D problem has now become a challenge in 3-D charge distribution optimization [2]. We study how the added (3-dimensional) spatial dependency affects the total charge distribution along the nanotube, and determine the extent of uniformity of charge distribution along the added spatial dimension (direction of the nanotube). The relation between optimal energy storage and charge distribution is also examined. To carry out this analysis, we have developed a 3-D molecular dynamics modeling simulator which incorporates Newton's classical charge interaction within the nanotube forest lattice. In this simulation, the electrons in the lattice are treated as classical particles, except that they have a unique linear energy dispersion relation. The results obtained using this simulation tool allow us to better assess the potential of carbon nanotube in enhancing energy storage capability of the ultracapacitor. [1] Joel Schindalls, "The charge of ultracapacitors," IEEE Spectrum, November 2007. [2] T. Yamada and D. K. Ferry, Phys. Rev. B 47, 6416 - 6426 (1993).

#### 10:45 AM P6.7

**Nanoporous Gold Electrodes Illustrate Important Supercapacitor Design Principles.** David B. Robinson<sup>1</sup>, Chung-An Max Wu<sup>1</sup>, Benjamin W Jacobs<sup>1</sup>, Kim L Tran<sup>1</sup>, Markus D Ong<sup>1</sup> and Bonnie E Pierson<sup>2</sup>; <sup>1</sup>Sandia National Laboratories, Livermore, California; <sup>2</sup>Biomedical Engineering, North Carolina State University, Raleigh, North Carolina.

Electrochemical supercapacitors can store more energy than parallel-plate capacitors, and charge more rapidly than batteries, so they are potentially valuable for applications such as regenerative braking in electrified vehicles. Typical engineering materials for these devices, such as carbon aerogels and metal oxides, have very complicated structures and properties. Nanoporous gold formed by dealloying has a well defined pore structure and a chemically well understood surface, and is a test platform in which phenomena can be isolated and studied. By tuning device geometry, salt concentration, and monolayer structure in nanoporous gold electrodes, we can observe phenomena such as salt depletion and partitioning that affect performance. Comparison of results to the de Levie model for porous electrodes, with extensions that account for these phenomena, leads us to proposals for design improvements that may lead to performance enhancements in practical devices.

#### 11:00 AM P6.8

**The Influence of Pore Confinement on Conducting Polymer Ultracapacitors.** Mark E. Roberts, Bonnie McKenzie, James A Ohlhausen, Todd M Alam and Bruce C Bunker; Sandia National Laboratories, Albuquerque, New Mexico.

Ultracapacitors are energy storage devices combining the high power, rapid switching, and exceptional cycle life of a capacitor with the high-energy storage capabilities of a battery. Power sources based on ultracapacitors are emerging as the best option for applications requiring short power pulses, particularly when used in combination with conventional batteries. In order to maximize capacitance, switching speed, and power, materials for ultracapacitors need to incorporate conductive electroactive materials into high surface area structures that are engineered to provide optimal contact between redox-active sites and electrolytes.

Conducting polymer are well-suited to address these challenges owing to a wide array synthesis and processing methods which result in a variety of nanostructures and electrical behaviors. While conducting polymers have been shown to enhance the electrical performance of ultracapacitor electrodes, the charge storage mechanism is not well-understood. Our approach for improving the performance of ultracapacitors and understanding the storage mechanism involves integrating conducting polymers into engineered nanocomposite architectures. In this study, we electrochemically deposit conducting polymers, including polyaniline, polypyrrole and polythiophene derivatives, within porous alumina films to determine their electrical properties with the critical dimensions of pore size and polymer thickness. The interface and order of the polymer at the alumina interface is tailored using carboxylic acid-terminated self-assembled monolayers of the monomer, which also assist in initiating the polymerization from the pore wall. Cyclic voltammetry (CV), electrical impedance spectroscopy (EIS) and charge-discharge measurements are used to determine the electrical characteristics, which are shown to depend on the polymer structure and composition, as determined by scanning electron microscopy (SEM). Ion intercalation and the polymer oxidation state are briefly investigated using solid-state NMR and x-ray photoelectron spectroscopy (XPS), respectively. The systematic variation of the critical parameters, along with a complete electrical characterization, is necessary to determine the optimal length scales and structure of the conducting polymer for ultracapacitor electrodes.

#### **11:15 AM P6.9**

**Templated Nanoporous Materials as a New Route to Electrochemical Supercapacitors** Sarah Tolbert<sup>1</sup>, Bruce Dunn<sup>2</sup>, Torsten Brezesinski<sup>1</sup> and John Wang<sup>2</sup>; <sup>1</sup>Chemistry and Biochemistry, UCLA, Los Angeles, California; <sup>2</sup>Materials Science and Engineering, UCLA, Los Angeles, California.

Block-copolymer templating of inorganic frameworks provides a powerful way to produce structures with homogeneous 3-dimensional mesoscale porosity from a wide variety of materials. In this talk, we explore how these materials can be used to optimize capacitive energy storage in electrochemical supercapacitors. We begin by examining hierarchical materials synthesized through templating of preformed titania nanocrystals. These studies lay down a simple set of architectural design rules for optimizing pseudocapacitive energy storage. We then move to nanoporous versions of layered oxides such as MoO<sub>3</sub> or Nb<sub>2</sub>O<sub>5</sub>. This allows us to explore the role of more traditional intercalation reactions in nanoscale pseudocapacitance. The results demonstrate how nanoscale porosity can increase power density while maintaining energy density in nanostructured transition metal oxides.

#### **11:30 AM P6.10**

**Designing Porous Silicon Nanowires for High Performance Electrochemical Capacitors** Jang Wook Choi, James McDonough and Yi Cui; MSE, Stanford University, Stanford, California.

Electrochemical capacitors (ECs) physically store electrical charges in electrical double layers (EDLs) by electrostatic forces between electrolytes and electrodes. Recently, ECs have attracted a remarkable attention due to their capabilities of operating at higher charge/discharge rates and recycling wasted energy. Despite these advantages, applications of the ECs have been limited owing to their lower energy densities, especially compared to those of batteries. However, the energy densities have been improved significantly by developing electrodes with larger surface area, constructing better electrode designs, finding more stable electrolytes and combining different charge storage mechanisms such as electrochemical reaction in the bulk of the electrodes. Here, we demonstrate that porous silicon nanowires (pSiNWs), where pores are generated by electrochemical process of Li ion insertion and extraction, increase the energy density by about ten times compared to the existing porous carbons, with still maintaining high power capability. The pore generation method by the Li electrochemical reaction not only provides an electrode platform for the high performance ECs, but also suggests a way of controlling pore size in a sub-nanometer scale, even at post-synthesis stages. Detailed EC performance including electrolyte dependence and cycle life will be also discussed.

#### **11:45 AM P6.11**

**Multilayer ALD Processing Sequence for MIM Capacitors Fabricated inside Anodic Aluminum Oxide Nanopore Templates for Energy Storage Applications.** Parag Banerjee<sup>1</sup>, Israel Perez<sup>1</sup>, Laurent Henn-Lecordier<sup>1</sup>, Sang Bok Lee<sup>2</sup> and Gary W Rubloff<sup>1,3</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; <sup>2</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland; <sup>3</sup>Institute for Systems Research, University of Maryland, College Park, Maryland.

Metal-Insulator-Metal (MIM) capacitors store charge via dielectric polarization of the insulator film. Since this process is extremely fast ( $\sim 10^{-15}$  seconds for electronic polarization), charging and discharging can be rapid if designs attain short RC time constants. MIM capacitors are extremely attractive for storing energy in applications that require high burst power, such as Hybrid Electronic Vehicles (HEV), but higher energy density is needed in MIM devices as well. We have taken a significant step in this direction by combining two fundamentally different nanotechnology processes to achieve economical, high density, 3-dimensional MIM capacitors with a capacitance per unit planar area of  $96\mu\text{F}/\text{cm}^2$  - one of the highest reported in literature. This represents a major increase in energy density of electrostatic capacitors without reduction of power or charge/discharge rate. First, we use self-assembly in anodic aluminum oxide (AAO) templates to create massive self-assembled arrays of highly uniform hexagonally arranged nanopores 80nm wide and up to 10μm deep with an aspect ratio 125 on the surface of high purity aluminum sheets. The surface area enhancement achieved due to the 3D pore structures is around 100X but can be increased to over 300X easily. Into these pores we deposit metal (TiN), insulator (Al<sub>2</sub>O<sub>3</sub>) and metal (TiN again) using atomic layer deposition (ALD). ALD has proved to be the perfect process for depositing thin films inside high aspect ratio structures, conformally and precisely, to achieve self-aligned nanodevices. The integrity of the multilayered structures is verified by SEM, TEM and EDX. We have then used simple

lithography steps to build Al metal electrodes over these capacitor structures, where each capacitor consists of a parallel array of  $\sim 10^6$  MIM nanocapacitors. Electrical measurements confirm our theoretical calculations for capacitances, where a 1 $\mu\text{m}$  deep pore yields a capacitance of 9.9 $\mu\text{F}/\text{cm}^2$  and a 10 $\mu\text{m}$  deep pore has a capacitance of 96 $\mu\text{F}/\text{cm}^2$ . To realize the practical benefit of this advance, we have begun to explore a variety of mechanisms that may degrade breakdown fields and leakage currents, including interface chemistry and structure at AAO/ALD and M/I/M interfaces and nanoscale electric fields arising from detailed AAO and ALD profiles. These results show that self-assembled AAO nanopore templates combined with highly controlled multilayer ALD achieves self-aligned nanostructure arrays that promise both high power and high energy density to fill critical gaps in today's portfolio of devices for electrical energy storage.

#### SESSION P7: Organic/Hybrid Solar Cells

Chairs: Harry Atwater and Paul W. M. Blom

Thursday Afternoon, April 16, 2009

Room 2022 (Moscone West)

##### 1:30 PM P7.1

**Energy-level Tuning in Polymer:Fullerene Bulk Heterojunction Solar Cells.** Paul W.M. Blom<sup>1,2</sup>, Martijn Lenes<sup>1,3</sup>, Floris Kooistra<sup>1</sup>, Kees Hummelen<sup>1</sup>, Mauro Morana<sup>4</sup> and Cristoph Brabec<sup>3</sup>; <sup>1</sup>Holst Centre, Eindhoven, Netherlands; <sup>2</sup>Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands; <sup>3</sup>Dutch Polymer Institute, Eindhoven, Netherlands; <sup>4</sup>Konarka Austria, Linz, Austria.

In order to further improve the efficiency of polymer:fullerene based bulk heterojunction solar cells at present two strategies are pursued: first, the light absorption of the polymer donor phase can be enhanced by lowering the band gap. Secondly, the open-circuit voltage can be increased by raising the LUMO of the fullerene acceptor phase. Here we address recent progress on both approaches. The charge transport and photogeneration in solar cells based on the low bandgap conjugated polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and fullerenes is studied. The efficiency of the solar cells is limited by a relatively low fill factor, that contradicts with the observed good and balanced charge transport in these blends. Intensity dependent measurements display a recombination-limited photocurrent, that originates from the short lifetime of the bound electron-hole pairs at the donor-acceptor interface. The LUMO of fullerene based acceptors can be raised using higher fullerene adducts.<sup>1</sup> We have investigated the performance of solar cells based on a range of bis- and tris fullerenes. In some cases the electron transport in the mixture of isomers is trap-limited, thereby limiting the performance of the solar cells. 1 M. Lenes et al., *Adv. Mat.* (2008)

##### 2:00 PM P7.2

**A Series of New Fullerene-derivative Electron Acceptors Aimed at Improvement in the Power Conversion Efficiency of Organic Photovoltaic Devices.** Kees Hummelen<sup>1</sup>, David F Kronholm<sup>2</sup> and Alexander B Sieval<sup>2</sup>; <sup>1</sup>University of Groningen, Groningen, Netherlands; <sup>2</sup>Solenne BV, Groningen, Netherlands.

A key research objective in bulk heterojunction organic photovoltaics remains improvement in power conversion efficiency (PCE), which today stands at 5% - 6%. One strategy for improvement of PCE is increasing the open circuit voltage (Voc), which is determined by the difference between HOMO (donor) and LUMO (acceptor) energies. The Voc can be optimized by tailoring the acceptor LUMO to the donor LUMO energy to the balance point of minimal energy loss and, at the other hand, still enough driving force for electron transfer. This strategy optimizes PCE through increasing the VOC, with potentially little to no changes required for other device or processing parameters. Multiply substituted fullerene derivatives (bis[60]PCBM), showed the viability of this approach, and allowed improvements in Voc and PCE of ca. 20% over P3HT:PCBM devices. We will address the present status of theoretical views on the balance point for the LUMO energy difference and we present further advances in tailoring the n-type LUMO energy, based on similar techniques and provide improved understanding of the approach of using multiply substituted fullerene-derivative n-type materials in bulk heterojunction organic photovoltaics.

##### 2:15 PM P7.3

**Correlation of Interfacial Composition and Bulk Morphology to Device Performance in Organic Bulk Heterojunction Solar Cells.** R. Joseph Kline<sup>1</sup>, David Germack<sup>1</sup>, Calvin Chan<sup>3</sup>, Behrang Hamadani<sup>3</sup>, Lee Richter<sup>2</sup>, David Gundlach<sup>3</sup>, Dan Fischer<sup>4</sup>, Michael Toney<sup>5</sup> and Dean DeLongchamp<sup>1</sup>; <sup>1</sup>Polymers Division, NIST, Gaithersburg, Maryland; <sup>2</sup>Surface and Microanalysis Science Division, NIST, Gaithersburg, Maryland; <sup>3</sup>Semiconductor Engineering Division, NIST, Gaithersburg, Maryland; <sup>4</sup>Ceramics Division, NIST, Gaithersburg, Maryland; <sup>5</sup>SSRL, Menlo Park, California.

Organic and hybrid inorganic/organic photovoltaic cells promise to drop solar energy costs low enough to compete with conventional technologies such as coal. Power conversion efficiencies up to 5.4% have been obtained and optimized materials and processing methods could potentially double that. Direct measurements of the morphology of bulk heterojunction (BHJ) blends are critical to future efficiency improvements. We have developed strategies to measure the orientation, distribution and dimension of morphological features in materials for organic thin film transistors (OTFTs) and photovoltaic devices that have led to rational guidelines for the design of new polymeric materials and processing techniques for the preparation of OTFTs. By employing the Near Edge X-Ray Absorption Fine Structure (NEXAFS) and ultra-violet variable angle spectroscopic ellipsometry (UV-VASE) in combination with grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM) we have developed models of interfacial composition and morphology and the vertical composition of a poly(3-hexylthiophene) (P3HT) : [6,6]-phenyl-C61-butyl acid methyl ester (PCBM) BHJ. This multi-platform approach is necessary to address the complex

morphology of the BHJ and to account for the optical anisotropies and resultant diffuse scattering of incident photons of technologically relevant films. Our approach also allows for the correlation of direct physical measurements with model-dependent methods that can be extended to provide *in situ* measurements of functional OPV devices. We will describe our ongoing efforts to correlate the electrical performance of P3HT/PCBM blend devices to measurements of interfacial composition and morphology and bulk morphology. These results, which demonstrate that by lowering the surface energy of the bottom contact (anode for the OPV device) causes this interface to be enriched in P3HT, but that for technologically relevant film thicknesses has no effect on the overall device performance or top contact (cathode) interface in both OTFT and OPV devices. The implications for PV device design, HTL design and interpretation of OTFT device results to evaluate morphological or compositional phenomena will also be discussed in the context of composition enrichment due to surface energy.

#### 2:30 PM P7.4

**Electron Tomography Image the 3D Nanostructure of Organic Solar Cells.** B. Viktor Andersson<sup>1</sup>, Anna Herland<sup>1</sup>, Sergej

Masich<sup>2</sup> and Olle Inganäs<sup>1</sup>; <sup>1</sup>Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden;

<sup>2</sup>Department of Cell and Molecular Biology, Karolinska Institutet, Stockholm, Sweden.

Polymer solar cells show potential for cheap energy conversion. However, the devices produced must be improved in terms of power conversion efficiency (PCE) to be competitive to silicon devices. The morphology of the active layer is of importance in this matter, and the possibility to control the morphology. The active layer in a polymer solar cell consists of a blend of electron donors and acceptors. Usually a polymer is used as main photon absorber and electron donor, and a fullerene derivative, PCBM, as electron acceptor. The electron acceptor is used to facilitate the dissociation of the exciton, produced upon excitation of the polymer. This can be achieved if the donor and acceptor are located no further from each other than the exciton diffusion length, which is typically 5-10 nm. Consequently there is a demand for a large interfacial area between the two species for efficient charge carrier generation. At the same time the produced free charges need to be collected efficiently at the electrodes in a well working cell. Thus continuous networks of the two phases are needed for good charge transportation. These two demands must be combined to produce efficient polymer solar cells. In order to be able to control the morphology of the active layer blend the possibility to visualise the same is crucial. So far the main effort in this area has been put on surface visualizing techniques, such as atomic force microscopy and scanning electron microscopy. Cross sectional studies have been performed with the help of scanning electron microscopy. Transmission electron microscopy, with which a projection of the film is produced, has also been used. Common for these techniques is that they do only show two dimensional images of a surface, be it the actual surface of a film or the surface of a cross section. In electron tomography several TEM images taken with the sample rotated at different angles are combined to form a reconstruction of the sample in all three spatial dimensions, while the resolution is better than 10 nm in the images. This is beneficial as it is the full morphology that is of importance for the behaviour of the solar cell. We have performed electron tomography on films used as active layers in polymer solar cells. The blends investigated consisted of a mixture of APFO-3 and PCBM in different weight ratios. The reconstructions clearly show a contrast difference due to the different scattering characteristics of the two materials. This allows us to display the morphology in three dimensions and compare the nanostructure of the different stoichiometries.

#### 2:45 PM P7.5

**Optically Limited Efficiency of Solid-state Dye Sensitized Solar Cells.** David M Huang<sup>1</sup>, Henry J Snaith<sup>2</sup>, Markus Kaiser<sup>4</sup>,

Michael Graetzel<sup>3</sup>, Klaus Meerholz<sup>4</sup> and Adam J Moule<sup>1</sup>; <sup>1</sup>Chem. Eng. and Mat. Sci., UC Davis, Davis, California; <sup>2</sup>Clarendon Laboratory, Department of Physics, University of Oxford, Oxford, United Kingdom; <sup>3</sup>Institut des Sciences et Ingenierie Chimique, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland; <sup>4</sup>Institut für Physikalische Chemie, Universität zu Köln, Köln, Germany.

The efficiency of a photovoltaic device is limited by the portion of solar energy that can be captured. We measure the optical properties of the various layers in solid-state dye sensitized solar cells (ss-DSCs) and use the measured optical properties to model spectral light absorbance in these devices. We use spectroscopic ellipsometry to determine the complex refractive index of each of the various layers in a ss-DSC. Each ellipsometry fit is verified by comparison to a transmission spectrum. The complexities of pore filling and wetting are discussed with respect to changes on the ellipsometric data. Scanning electron microscopy (SEM) is used to determine pore filling in ss-DSC layers. Scanning energy dispersive x-ray spectroscopy (EDX) is shown to be an effective method for determining pore filling. Accurate effective medium optical constants for each layer are presented and the material limits under which these optical constants can be used are discussed. We then use the optical transfer-matrix method and the measured optical constants to quantify the spatial distribution of light in ss-DSCs and thereby calculate the absorption-limited maximum external quantum efficiency (EQE) and short-circuit current density (Jsc) for various wavelengths and layer thicknesses. Comparisons with experimental measurements of ss-DSCs containing either the ruthenium-based Z907 dye or the organic D149 dye indicate that the internal quantum efficiency (IQE) of the devices is around 60% and approximately independent of wavelength and dye type. The model calculations also demonstrate significant optical losses due to absorption by the spiro-MeOTAD and titanium oxide, particularly at lower wavelengths near the absorption maxima of the dyes. The change over time of the absorption spectrum of spiro-MeOTAD at long wavelengths, due to oxidation, is also shown to have a detrimental effect on device efficiency. The more absorptive D149 dye is found to perform significantly better than the Z907 dye for all device thicknesses. Small improvements in device performance of around 5% are shown to be achievable by minimizing optical losses through varying the thicknesses of the various layers.

#### 3:30 PM \*P7.6

**Light Concentration In Solar Cells using Metallic and Dielectric Nanostructures.** Peter Peumans, Electrical Engineering, Stanford University, Stanford, California.

The efficiency of many types of solar cells depends sensitively on the ability to guide and concentrate light. I will discuss two approaches to light concentration on the nanometer scale for thin-film solar cells. First, I will show how engineering of the dielectric constant of a thin-film solar cell can be used to achieve light concentration approaching the thermodynamic limit. Structures were designed by rigorous optimization of periodic photonic structures and their operation can be understood as effective coupling of incident light into quasi-guided modes over a broad spectral range. A theoretical analysis confirms that the best possible enhancement of optical absorption in the wave regime is equal to that obtained in the geometric optics regime. In the second part of my talk, I will show how metal nanostructures can be used to achieve light concentration on very small length scales. This approach has merit for solar cells whose active region is only a few nanometer wide, as is the case for organic solar cells. The relation between the degree of light concentration and acceptance angle of a solar cell in the wave regime will be compared to the classical result obtained in the geometric optics regime.

#### **4:00 PM \*P7.7**

**Controlling Morphology In Organic Bulk-Heterojunction Solar Cells.** Klaus Meerholz<sup>1</sup> and Adam Moule<sup>2</sup>; <sup>1</sup>University of Cologne, Cologne, Germany; <sup>2</sup>Chemical Engineering and Materials Science, University of California at Davis, Davis, California.

Conjugated polymers, polythiophenes in particular, are being intensively studied for use in polymer/fullerene bulk-heterojunction photovoltaic (PV) devices. In these devices, a bi-continuous morphology with electronic pathways for holes and electrons is required. A large body of anecdotal/imperical information exists about how to manipulate the morphology and what morphological features lead to a high efficiency bulk-heterojunction PV device. In this contribution, we present an in-depth study of controlling and quantifying the morphology by various means, e.g. by pre-forming particles by addition of a non-solvent. The influence of various annealing protocols (thermal, solvent, current) is investigated. In addition, we compare two polythiophene isomers to determine which parameters made these two polymers more and less suitable for use in bulk-heterojunction solar cells.

#### **4:30 PM P7.8**

**Direct Formation of Sulfidic Nanoparticles in Semiconducting Organic Matrices for Hybrid Photovoltaics** Eugen Maier<sup>1</sup>, Thomas Rath<sup>1</sup>, Sonja Larissegger<sup>1</sup>, Robert Saf<sup>1</sup>, Roland Resel<sup>2</sup>, Dieter Meissner<sup>3</sup>, Franz Stelzer<sup>1</sup> and Gregor Trimmel<sup>1</sup>; <sup>1</sup>ICTM, Graz Technical University, Graz, Austria; <sup>2</sup>Institute of Solid State Physics, Graz University of Technology, Graz, Austria; <sup>3</sup>Department of Materials Science, Tallinn University of Technology, Tallinn, Estonia.

Control of the 3D-architecture of the active layer in bulk heterojunction organic solar cells is one of the major aspects for high efficiencies. In this contribution, we present a novel method to prepare nano-scaled inorganic semiconductors within a matrix of a conjugated polymer directly, resulting in a network of organic donor- and inorganic acceptor phase. As prepared organic-inorganic semiconductor blends are used as active layers in bulk heterojunction-type hybrid solar cells. By the reaction of suitable inorganic metal salts (e. g. Zn(Ac)<sub>2</sub>) with a sulphur source (e. g. thioacetamide (TAA)) within a matrix consisting of a conjugated organic polymer (e.g. poly-para-phenylene-vinylene (PPV)), sulfidic inorganic semiconductors are formed (e.g. ZnS). Moderate temperatures (~ 200° C) are applied to decompose the sulphur source. By a proper choice of processing conditions a nano-structured three-dimensional network of the two components is accessible. Various combinations of materials are possible. Our group prepared chalcopyrite-type (e.g. CuInS<sub>2</sub>) semiconductors dispersed in PPV-type polymers. Formation of the inorganic phase was monitored online by XRD; in-situ mass spectrometry was performed to monitor the process. The chemical composition of the layers was analyzed by electron microscopy (SEM-EDX, TEM). Hybrid solar cells containing active layers of as prepared blends were fabricated.

#### **4:45 PM P7.9**

**Measurements and Modeling of Charge-carrier Mobilities and Recombination Lifetimes in Conjugated Polymer/Fullerene Bulk-heterojunction Solar Cells Prepared Under Different Conditions.** Bertrand Tremolet de Villiers and Benjamin J Schwartz; Chemistry and Biochemistry, UCLA, Los Angeles, California.

Driven by current global energy concerns, research in new types of solar cells has received increasing attention. Polymer-based, organic photovoltaics offer a cheap, flexible, and versatile alternative to traditional, silicon-based solar cells, but their maximum efficiency, currently 5-6%, must be improved before they can become widely used. Film morphology plays an important role in the performance of a conjugated-polymer/fullerene bulk-heterojunction solar cell and can be controlled to some extent by the device fabrication parameters, e.g. solvent choice, and post-fabrication processing such as thermal annealing. Understanding the detailed transport characteristics of these types of photovoltaics may lead to the development of better materials and solar cell fabrication processes, resulting in new designs and materials that will lead to increased performance. We used a recently-developed spectroscopic method, photo-induced charge carrier extraction by linearly increasing voltage (photo-CELIV), to investigate charge-carrier mobility and recombination kinetics in blend films of poly[3-hexyl thiophene] (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). In photo-CELIV, a short flash of light from a laser creates charge carriers within the thin organic film, the carriers are given time to recombine, and then the remaining carriers are extracted by a bias ramp after an adjustable delay time. Modeling of the current transients allows one to extract mobility values for the charge carriers as well as the recombination lifetimes of the photo-generated carriers within the solar cell. We investigated devices prepared from different solvents as well as treated under different post-fabrication processing conditions. Solutions were made using either ortho-dichlorobenzene (ODCB) or a mixture of ODCB and diiodooctane as the solvent. The use of diiodooctane has been shown to improve device performance. In addition, some spincoated films of P3HT/PCBM were left to dry in a saturated atmosphere of ODCB, while others were thermally annealed on a hotplate; both processes have also been shown to improve device efficiency. We correlate our calculated mobilities and lifetimes with the device preparation and processing conditions, and we show that

charge transport is affected by film morphology and thus is directly related to the efficiency of the solar cell.

#### SESSION P8: Synthesis and Fabrication Routes for 3D Architectures

Chair: Jeffrey Long

Friday Morning, April 17, 2009

Room 2022 (Moscone West)

##### **8:30 AM \*P8.1**

**The Electrochemical Synthesis: A Powerful Tool to Produce Nanostructured Electrodes for Battery.** Philippe Poizot, LRCS, Universite de Picardie Jules Verne, Amiens, France.

Nano-sized and nano-structured materials are getting great interest in most of today's scientific research activities. In the particular field of Li-ion batteries R&D, nano-sized positive or negative electrode materials offer attractive electrochemical characteristics over classical bulk materials.<sup>1</sup> This includes occasionally an unexpected reactivity<sup>2</sup>, a better accommodation of the materials strains associated with the lithium insertion/extraction, a shorter path length for ionic and electronic transport and finally a higher active material/electrolyte contact. The latter interface can even be improved by acting on the current collector surface. Nano-architected current collectors offer higher contact area than conventional 2D-substrate. As a result, for an equivalent thickness, the amount of active material is much higher on a nano-structured current collector. Second, the cycling performances of active materials are usually improved owing to the electronic contact reinforcing together with the significant decrease of diffusion length. Moreover, in the case of reacting active alloys (or metals) towards Li, the nano-structures act also as a buffer, so that the well-known cracking caused by a strong volume variation during the cycling can be partially limited.<sup>3</sup> Among the various methods for the preparation of nanoparticles, the electrochemical synthesis appears as an economical and convenient choice since it is easy to operate and requires relatively inexpensive equipments. Basically, the composition, microstructure and morphology of the films could be tailored by controlling the applied potential and/or current, the bath composition and the mass transport conditions. Moreover, since the pioneer's works initiated by C.R. Martin<sup>5,6</sup> in the mid-90s, high quality nanostructured electrodeposits can also be produced thanks to "the template-assisted synthesis". Therefore, we have developed advanced strategies for the electrodeposition of nanometer-sized particles of active compounds vs. Li but also alternative approaches to produce nano-architected current collectors without using any nanoporous template. References: 1.A.S. Arico, P. Bruce, B. Scrosati, J-M. Tarascon, W. Van Schalkwijk, *Nature Materials*, 4, 366 2. 2.P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J-M Tarascon, *Nature (London)*, 407, 496 (2000). 3.M. Winter, J.O. Besenhard, *Electrochim. Acta*, 45, 31 (1999). 4.C.R. Martin, *Science* 266, 1961 (1994). 5.C.R. Martin, *Chem. Mat.* 8, 1739 (1996).

##### **9:00 AM P8.2**

**Abstract Withdrawn**

##### **9:15 AM P8.3**

**Cobalt Oxide Aerogels Prepared with Epoxide Synthetic Route Exhibiting Excellent Supercapacitor Properties.** Shih-Yuan Lu, Te-Yu Wei, Chi-Chang Hu and Chun-Hung Chen; Dept. of Chemical Engineering, National Tsing-Hua University, Hsin-Chu, Taiwan.

Cobalt oxide aerogels of excellent supercapacitor properties (the best for cobalt oxides to our best knowledge), high specific capacitances (623F/g at 25mV/s from -0.1 to 0.55V in 1M NaOH), excellent reversibility, and outstanding cycle stability (96% remaining capacitance after 1000 cycles), were synthesized with the epoxide addition procedure for the first time by using cobalt nitrate as the precursor. Cobalt oxide is a promising low cost transition metal oxide targeted for supercapacitors of the asymmetric type, and the epoxide synthetic route enables preparation of transition metal oxide aerogels from low cost and stable metal salts instead of the much more expensive, moisture and heat sensitive metal alkoxides. This work is the first successful example for producing cobalt oxide aerogels from a cobalt salt. The resistances to the electrolyte diffusion in the cobalt oxide aerogel, xerogel, and microstructure templated from an MCM-41 were investigated with the electrochemical impedance spectroscopy analysis. Our aerogel products, possessing mainly mesopores, exhibited among the three structures the lowest resistance for the electrolyte diffusion, which is an important advantage for supercapacitor applications. This demonstrated the advantage of mesopores over micropores in boosting the supercapacitor performance. The decay of specific capacitance of our aerogel product at scan rates ranging from 2 to 50 mV/s was 27%, much lower than that achieved by the microstructured cobalt oxide from the MCM-41 template (44% from 2 to 50 mV/s). The development of the present work makes possible the low cost production of high performance supercapacitors of the asymmetric type.

##### **9:30 AM P8.4**

**Hybrid RuO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> Nanocomposites for Ultracapacitors.** Michael Todd Brumbach, Todd Alam, Paul Kotula, Ralph Tissot and Bruce Bunker; Sandia National Laboratories, Albuquerque, New Mexico.

Ultracapacitors, or electrochemical capacitors, achieve very high specific capacitances by storing charge not only in the electrical double layer but via redox reactions that occur in the bulk material adjacent to the electrolyte. Requirements for optimized ultracapacitors include: 1) oxidation-reduction reactions in the bulk material that occur at a redox potentials that fall within the stability window of the electrolyte, 2) efficient transport of both electrons and charge-compensating ions within the bulk, and 3) materials architectures that maximize material:electrolyte contact and minimize electron and ion transport distances. In terms of redox activity and charge mobility, ruthenium oxide is often considered to be the "gold standard" among oxides. However, as ruthenium oxide is much rarer and more expensive than gold, it has seen limited utility in commercial devices. The purpose of this

investigation is to explore the extent to which ruthenium oxide can be replaced in oxide nanostructures without compromising performance. In this study, we explored solution synthesis methods for creating intimate mixtures of RuO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> at the nano-scale. The resulting nanocomposites have been extensively characterized in terms of composition, nanostructure, and performance. The results show that the Nb<sub>2</sub>O<sub>5</sub> end member exhibits a high specific capacitance. However, transmission electron microscope results suggest that this capacitance is associated with the fact that the Nb<sub>2</sub>O<sub>5</sub> material has a uniform, high surface area architecture containing interconnected niobate clusters that are smaller than 5 nm in diameter. In other words, the Nb<sub>2</sub>O<sub>5</sub> has no redox activity, but functions as a double layer capacitor. The RuO<sub>2</sub> end member has a similar nano-architecture, but has a much larger capacitance due to redox activity in the bulk. Interestingly, mixtures of the two oxides can result in capacitance values that can be greater than that of bulk RuO<sub>2</sub>, especially at high charge-discharge rates. In fact, composites containing 2Nb<sub>2</sub>O<sub>3</sub>:RuO<sub>2</sub> have a capacitance that is four times greater per Ru atom than bulk RuO<sub>2</sub>. Proton NMR results suggest that the range of performance characteristics exhibited in the mixed oxide systems can be rationalized by the distribution of hydroxyl groups within the oxide hosts. The results are discussed in terms of the presence of nanodomains similar to those found in layered clay-like minerals such as HTiNb<sub>2</sub>O<sub>5</sub>. It appears that these domains can simultaneously support both electron and proton transport in response to redox reactions on the ruthenium cations.

#### 9:45 AM P8.5

**Aligned LiFePO<sub>4</sub> Nanorods Array: A Novel Cathode for High Performance Lithium Battery.** Xiangyang Kong, Shanghai Jiao Tong University, Shanghai, China.

Since the pioneering work of Goodenough et al. LiFePO<sub>4</sub> (olivine) attracted considerable interest for application as a cathode material in Li-ion batteries with improved safety and reduced cost. However, the poor electrical conductivity of LiFePO<sub>4</sub> is a crucial issue to be addressed either by doping with supervalent cations or by carbon additives, which may also generate iron phosphides or phosphocarbides at the surface. Various strategies of conductivity promoting have also raised conflicting debate in the literature, and eventually, the strain generated during the charge/discharge needs to be considered as another factor controlling the performance of olivine structures. Some theoretical calculations indicate that the phase conversion of LiFePO<sub>4</sub>/FePO<sub>4</sub> with Li<sup>+</sup> ions moving parallel to the b-axis of the olivine lattice. Based on this suggestion, we proposed that alignment of nanorod arrays of LiFePO<sub>4</sub> would be shorter electronic conduction path helpful in reducing ohmic resistance within the aligned nanorod along the growth direction of the b-axis. In our case, high crystalline nanorods of LiFePO<sub>4</sub> have been prepared without any impurities by using hydrothermal process. The alignment of LiFePO<sub>4</sub> nanorods was conducted under the magnetic field up to 2T into the oriented array along the b-axis. The battery with the aligned nanorods cathod exhibited the highest electrochemical reactivity among the prepared samples, and the discharge capacity was about 160mA h/g measured at a current density of 17 mA/g.

#### 10:30 AM P8.6

**Fabrication of Three Dimensional Photovoltaic Devices Based on Semiconducting Coaxial Nanocable Arrays.** Kai Wang<sup>1</sup>, Zhongming Zeng<sup>1</sup>, Jiajun Chen<sup>1</sup>, Weili Zhou<sup>1</sup>, Yong Zhang<sup>2</sup>, Yanfa Yan<sup>2</sup>, John Pern<sup>2</sup> and Angelo Mascarenhas<sup>2</sup>; <sup>1</sup>AMRI/Chemistry, Advanced Materials Research Institute/UNO, New Orleans, Louisiana; <sup>2</sup>National Energy Renewable Laboratory, Golden, Colorado.

We previously presented a successful synthesis of large-area, vertically aligned, air-stable II-VI semiconducting coaxial nanocable arrays directly grown on transparent conductive oxide (TCO) glass substrates. Here, we report photovoltaic device fabrication based on such three dimensional nanocable array by depositing-and-etching process with a photoresist. The photovoltaic properties of the devices were also investigated. This study provides an experimental demonstration for directly integration of a three dimensional nano-architecture on TCO substrate into a novel and low cost photovoltaic device that leads to high efficient solar energy harvesting.

#### 10:45 AM P8.7

**Si Thin Film Driven Self-Assembly of 2D and 3D Structured Devices.** Xiaoying Guo<sup>1</sup>, Huan Li<sup>3</sup>, Bok Yeop Ahn<sup>1</sup>, Eric B Duoss<sup>1</sup>, Jimmy K Hsia<sup>3</sup>, Jennifer A Lewis<sup>1,4</sup> and Ralph G Nuzzo<sup>1,2</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois; <sup>2</sup>Department of Chemistry, University of Illinois at Urbana Champaign, Urbana, Illinois; <sup>3</sup>Department of Mechanical Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois; <sup>4</sup>Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois.

Fabrication of three dimensional (3D) patterned structures in the μm-to-mm range is extremely challenging due to the inherently two dimensional (2D) nature of wafer-based fabrication. Self-assembly, or self-folding of planar patterned membranes provides a promising method to solve this problem. In this research, we demonstrate a complimentary and somewhat more easily implemented strategy, making use of self-assembly processes driven by the wetting interactions. A mechanics model based of the theory of thin plate folding has been developed to identify the critical conditions of self-folding for different 2D geometrical shapes. We use this strategy to construct specifically designed microscale silicon objects for assembly into spheroidal, as well as other simple non-planar shaped objects that could integrate into fully functional photovoltaic (PV) junction devices.

#### 11:00 AM P8.8

**ALD Conformality and Optimization in Ultrahigh Aspect Ratio Nanopores for Electrical Energy Storage Nanodevices.** Laurent Lecordier<sup>1</sup>, Erin Robertson<sup>1</sup>, Israel Perez<sup>1</sup> and Gary Rubloff<sup>1,2</sup>; <sup>1</sup>Department of Materials Science and Engineering,

University of Maryland, College Park, Maryland; <sup>2</sup>Institute for Systems Research, University of Maryland, College Park, Maryland.

Paralleling the trend in electronic devices, 3D architectures for energy devices require nanostructures with increasingly high aspect ratios as well as nano-scale feature size. Fabrication of such structures requires highly conformal deposition processes. Atomic layer deposition (ALD) is replacing physical and chemical vapor deposition methods because of ALD's exceptional conformality and thickness control. We are applying ALD to produce multilayer devices in nanopores with ultra-high aspect ratios (up to 1000:1) formed during anodic oxidation of aluminum to produce anodic aluminum oxide (AAO). The nanopores have diameters 15-100nm and depths 1-30μm, with uniform dimensions and spacing. As nanostructures are formed in the nanopores, extremely high conformality is required and becomes more demanding as the nanopore volume is increasingly filled to complete the structures. To achieve precise control of nanostructure fabrication in AAO membrane templates, we have investigated conformality profiles of ALD layers deposited into AAO nanopores, focusing on TiO<sub>2</sub> as a high-K insulator sought for ultrahigh density electrostatic nanocapacitors. ALD employs alternating reactant exposures of organometallic precursors and oxidants, providing a self-limiting adsorption/reaction mechanism that is known to produce unprecedented uniformity and conformality, as well as thickness control on an atomic scale. While uniform films can be achieved across a planar wafer with the correct recipe of saturating doses and sufficient purge times, saturation doses become insufficient when translated to an ultra-high aspect ratio nanopore, caused by significantly larger surface areas to be covered and the interplay between diffusion and surface reaction in ultrahigh aspect ratio nanostructures. We have adjusted ALD process recipes to optimize conformality in the nanopores while monitoring the consequences of higher precursor doses on across-wafer uniformity, anticipating that viable technologies will require conformal deposition profiles in nanopores across extended AAO substrates. SEM was used to measure pore diameters (40-80 nm) before and after the ALD deposition. The TiO<sub>2</sub> nanotubes were released by dissolution of the alumina template and examined via standard TEM. TEM and EDS profiles showed TiO<sub>2</sub> nanotubes having decreased wall thicknesses (10 nm to 3 nm) down the lengths of 1-10 microns nanotubes. By analyzing quantitative thickness profiles along the length of the nanotubes and by comparing this data to the uniformity across planar wafers, we were able to optimize the ALD process leading to better understanding and control of ALD conformality within the nanopores. In-situ real-time mass spectrometry was also explored to give a better understanding of the deposition kinetics between a 2-dimensional planar wafer and a 3-dimensional nanopore.

#### **11:15 AM P8.9**

**3D Multifunctional Micro/nanowire Materials.** Ming Su, NanoScience Technology Center, University of Central Florida, Orlando, Florida.

Controlled fabrication of 3D multifunctional materials is of great importance for many areas. We have used fiber-drawing method to produce fibrous building blocks of metals, semiconductors, long channels, and spikes, all with structural features at micro/nanometer scales. Such novel building blocks can be manipulated directly to form 3D ordered structures with defined size, arrangement, orientation, and materials multiplicity. The 3D structures with appropriate functions have been used as novel materials with superior thermal, surface and optical properties, which can either enhance the energy efficiency, or facilitate the heat energy transfer.

#### **11:30 AM P8.10**

**Three-dimensional Architected Micro Solid-Oxide Fuel Cells for Portable Power.** Bo-Kuai Lai, Hui Xiong, Alex Johnson and Shriram Ramanathan; School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy from hydrogen or hydrocarbon fuels directly into electrical energy at elevated temperatures. They have been considered as a promising energy alternative for applications ranging from large scale power plants to smaller scale ones, such as portable electronics, owing to high energy efficiency, high power density, and clean emissions. In recent years, micro SOFCs (uSOFCs) have particularly stimulated considerable attention owing to increasing demand for efficient power sources for mobile applications. The heart of uSOFCs is a microfabricated membrane that is consisted of ultrathin cathode, electrolyte, and anode layers. By taking advantage of well-established thin film deposition and microfabrication techniques, they could possibly be mass-produced at low cost. A significant challenge ahead for uSOFCs development is to realize uSOFC stacks in order to further increase power output from a uSOFC system. In a uSOFC stack, each individual uSOFC is stacked with bipolar plates, which integrate gas flow channels to separately supply gases to cathode and anode and are conductive to extract electric current from the uSOFCs. Therefore, it is critical for the interface of such stack to be gas-tight and thermomechanically stable with minimal electrical losses. In this work, experimental results towards achieving uSOFC stacks will be reported. High-quality Lanthanum Strontium Cobalt Ferrite (LSCF) ultrathin films have been synthesized by sputtering onto Yttria-stabilized Zirconia thin films and a detailed conductivity study has been carried out up to 700 °C. Microstructure evolution in LSCF ultrathin films has been studied through XRD and AFM to directly correlate with electrical transport measurements. We find that the appearance of micro-scale cracks in the cathode layer can affect the overall mechanical stability of the thin film fuel cell device structure. Our approach to fabricate three-dimensionally integrated fuel cells includes utilizing microfabrication techniques to create flow channels and through silicon vias - for guiding gas flow through bipolar plates utilizing semiconductor structures. Potential issues and possible fabrication approaches will be discussed in detail along with experimental results.

#### **11:45 AM P8.11**

**Microstructural Effects on Solid Oxide Fuel Cell Electrodes** Hsun-Yi Chen<sup>1</sup>, C. Kreller<sup>2</sup>, J. R Wilson<sup>3</sup>, S. Cronin<sup>3</sup>, S. A Barnett<sup>3</sup>, S. B Adler<sup>2</sup> and K. Thornton<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Chemical Engineering, University of Washington, Seattle, Washington; <sup>3</sup>Material Science and Engineering, Northwestern University, Evanston, Illinois.

Electrodes in solid oxide fuel cells (SOFCs) are responsible for the facilitation of electrochemical reactions and the concurrent transport of various species through different phases. Complex microstructures are necessary to obtain the desired multifunctionality required for effective electrochemical performance. However, transport and electrochemical models of SOFC electrodes have so far been limited by the lack of microstructural information. Utilizing our capability for acquiring three-dimensional (3D) microstructural data, we calculated tortuosity factors of experimentally determined 3D electrode microstructures with a range of volume fractions. We also performed 3D electrochemical simulations to analyze the thickness of the electrochemically active regions of microstructures in two-phase cathodes and to identify active three-phase boundaries in three-phase anodes. These analyses may provide useful guidance for microstructural designs in SOFC electrodes.



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